

Special Issue Reprint

Modeling and Simulation of Industrial and Environmental Processes with Membranes

Edited by
José M. Gozávez-Zafrilla

mdpi.com/journal/membranes

Modeling and Simulation of Industrial and Environmental Processes with Membranes

Modeling and Simulation of Industrial and Environmental Processes with Membranes

Guest Editor

José M. Gozávez-Zafrilla



Basel • Beijing • Wuhan • Barcelona • Belgrade • Novi Sad • Cluj • Manchester

Guest Editor

José M. Gozálvéz-Zafrilla

Institute for Industrial,

Radiophysical and

Environmental Safety

(ISIRYM)

Universitat Politècnica de

València

Valencia

Spain

Editorial Office

MDPI AG

Grosspeteranlage 5

4052 Basel, Switzerland

This is a reprint of the Special Issue, published open access by the journal *Membranes* (ISSN 2077-0375), freely accessible at: https://www.mdpi.com/journal/membranes/special_issues/Modeling_Mem.

For citation purposes, cite each article independently as indicated on the article page online and as indicated below:

Lastname, A.A.; Lastname, B.B. Article Title. <i>Journal Name</i> Year , Volume Number, Page Range.
--

ISBN 978-3-7258-8647-0 (Hbk)

ISBN 978-3-7258-8648-7 (PDF)

<https://doi.org/10.3390/books978-3-7258-8648-7>

© 2026 by the authors. Articles in this reprint are Open Access and distributed under the Creative Commons Attribution (CC BY) license. The reprint as a whole is distributed by MDPI under the terms and conditions of the Creative Commons Attribution-NonCommercial-NoDerivs (CC BY-NC-ND) license (<https://creativecommons.org/licenses/by-nc-nd/4.0/>).

Contents

About the Editor	vii
----------------------------	-----

Preface	ix
-------------------	----

José M. Gozávez-Zafrilla

Modeling and Simulation of Industrial and Environmental Processes with Membranes

Reprinted from: *Membranes* **2026**, 16, 225, <https://doi.org/10.3390/membranes16070225> 1

Alexandre Alentiev, Sergey Chirkov, Roman Nikiforov, Mikhail Buzin, Oleg Miloserdov, Victoria Ryzhikh, et al.

Structure-Property Relationship on the Example of Gas Separation Characteristics of Poly(Arylene Ether Ketone)s and Poly(Diphenylene Phtalide)

Reprinted from: *Membranes* **2021**, 11, 677, <https://doi.org/10.3390/membranes11090677> 6

Abdulrahman Alraeesi and Tracy Gardner

Assessment of Sieverts Law Assumptions and ‘n’ Values in Palladium Membranes: Experimental and Theoretical Analyses

Reprinted from: *Membranes* **2021**, 11, 778, <https://doi.org/10.3390/membranes11100778> 27

Run Shi, Huaiguang Xiao, Chengmeng Shao, Mingzheng Huang and Lei He

Study on the Influence of Geometric Characteristics of Grain Membranes on Permeability Properties in Porous Sandstone

Reprinted from: *Membranes* **2021**, 11, 587, <https://doi.org/10.3390/membranes11080587> 49

Konstantin Popov, Maxim Oshchepkov, Alexei Pervov, Vladimir Golovesov, Anastasia Ryabova, Maria Trukhina and Sergey Tkachenko

A Case Study of Calcium Carbonate Crystallization during Reverse Osmosis Water Desalination in Presence of Novel Fluorescent-Tagged Antiscalants

Reprinted from: *Membranes* **2022**, 12, 194, <https://doi.org/10.3390/membranes12020194> 69

José-Luis Díez, Vicente Masip-Moret, Asunción Santafé-Moros and José M. Gozávez-Zafrilla

Comparison of Artificial Intelligence Control Strategies for a Peristaltically Pumped Low-Pressure Driven Membrane Process

Reprinted from: *Membranes* **2022**, 12, 883, <https://doi.org/10.3390/membranes12090883> 84

Yanqiu Pan, Liu He, Yisu Ren, Wei Wang and Tonghua Wang

Analysis of Influencing Factors on the Gas Separation Performance of Carbon Molecular Sieve Membrane Using Machine Learning Technique

Reprinted from: *Membranes* **2022**, 12, 100, <https://doi.org/10.3390/membranes12010100> 102

Aleksandar Jokić, Ivana Pajčin, Nataša Lukić, Vanja Vlajkov, Arpad Kiralj, Selena Dmitrović and Jovana Grahovac

Modeling and Optimization of Gas Sparging-Assisted Bacterial Cultivation Broth Microfiltration by Response Surface Methodology and Genetic Algorithm

Reprinted from: *Membranes* **2021**, 11, 681, <https://doi.org/10.3390/membranes11090681> 116

Aleksandar Jokić, Nataša Lukić, Ivana Pajčin, Vanja Vlajkov, Selena Dmitrović and Jovana Grahovac

Kenics Static Mixer Combined with Gas Sparging for the Improvement of Cross-Flow Microfiltration: Modeling and Optimization

Reprinted from: *Membranes* **2022**, 12, 690, <https://doi.org/10.3390/membranes12070690> 133

Lu He, Aipeng Jiang, Qiuyun Huang, Yan Zhao, Chuang Li, Jian Wang and Yudong Xia Modeling and Structural Optimization of MSF-RO Desalination System Reprinted from: <i>Membranes</i> 2022 , 12, 545, https://doi.org/10.3390/membranes12060545	145
Lu He, Yudong Xia, Chuang Li, Aipeng Jiang, Yan Zhao and Fengling Xie Simulation and Operational Optimization of RO Based Desalination for Coal-Fired Power Plants' Wastewater Reprinted from: <i>Membranes</i> 2022 , 12, 478, https://doi.org/10.3390/membranes12050478	170
Marc Fill and Mirko Kleingries Modeling and Simulation of Either Co-Current or Countercurrent Operated Reverse-Osmosis-Based Air Water Generator Reprinted from: <i>Membranes</i> 2021 , 11, 913, https://doi.org/10.3390/membranes11120913	197
Minmin Jiang, Yuanyuan Zhang, Jie Zhang, Xingru Dai, Haixiang Li, Xuehong Zhang, et al. Model Evaluation of the Microbial Metabolic Processes in a Hydrogen-Based Membrane Biofilm Reactor for Simultaneous Bromate and Nitrate Reduction Reprinted from: <i>Membranes</i> 2022 , 12, 774, https://doi.org/10.3390/membranes12080774	210
Ephraim Bonah Agyekum, Christabel Nutakor, Ahmed M. Agwa and Salah Kamel A Critical Review of Renewable Hydrogen Production Methods: Factors Affecting Their Scale-Up and Its Role in Future Energy Generation Reprinted from: <i>Membranes</i> 2022 , 12, 173, https://doi.org/10.3390/membranes12020173	226

About the Editor

José M. Gozávez-Zafrilla

José M. Gozávez-Zafrilla is currently a Full Professor in the Department of Chemical and Nuclear Engineering at the School of Industrial Engineering of the Universitat Politècnica de València (UPV), where he is Academic Director of the Bachelor's degree in Chemical Engineering. He is a researcher at the Institute for Industrial, Radiophysical and Environmental Safety (ISIRYM). He obtained his degree in Industrial Engineering from UPV in 1991 and, in 1998, defended his doctoral thesis on membrane fabrication. He has developed his research career at UPV since then, with professional experience in thermal simulation, modeling, and optimization of industrial processes, chemical reactor engineering, and membranes for reverse osmosis and nanofiltration. His current and previous research interests include simulation and optimization across subjects such as membranes, membrane reactors, contact lenses, neural networks applied to industrial processes, and uncertainty and sensitivity analysis. His research activities have been carried out through various competitive projects, resulting in numerous articles in top journals. He has served as a coordinator of Master's courses in Chemical Engineering. He has been the guest editor of three MDPI journals on modeling and simulation applied to the membrane field.

Preface

This Reprint is a collection of research studies on the modeling and simulation of membrane processes. The aim of this Special Issue is to provide an overview of recent developments in modeling and simulation techniques applied to membrane processes and membrane-based systems. The contributions included in this volume illustrate the diversity of approaches currently used in the field, ranging from fundamental studies on membrane materials and transport mechanisms to advanced process simulations and optimization strategies for industrial applications.

The motivation behind this Special Issue is to highlight the growing importance of modeling and simulation as tools for accelerating the development and implementation of membrane technologies. By bringing together contributions from diverse areas of membrane science and engineering, the volume aims to provide a comprehensive perspective on current modeling practices and emerging trends shaping the field's future.

This volume is intended for researchers, engineers, and graduate students working in membrane science, chemical engineering, environmental engineering, and related disciplines. By presenting a collection of studies that spans fundamental modeling concepts and practical process applications, the Special Issue seeks to contribute to the continued advancement of membrane modeling and simulation methodologies.

José M. Gozávez-Zafrilla

Guest Editor

Editorial

Modeling and Simulation of Industrial and Environmental Processes with Membranes

José M. Gozálvarez-Zafrilla

Institute for Industrial Radiophysical and Environmental Safety (ISIRYM), Universitat Politècnica de València,
46022 Valencia, Spain; jmgz@iqn.upv.es

1. Introduction

Membrane technologies are a key technique in modern separation because of their flexibility and the intrinsic modularity of membrane processes, which can reduce energy consumption compared to conventional thermal separations and enable separations that are difficult to achieve with other processes [1–3]. That is why membrane processes are widely used in many industrial and environmental applications, such as desalination, water and wastewater treatment, gas separation, purification and product recovery, food and beverage processing, pharmaceutical and biotechnological operations, biomedical devices, membrane reactors, environmental remediation, energy-related technologies, and sensors. In all these fields, the use of membranes continues to evolve and expand.

In the membrane field, as in many other scientific and engineering disciplines, modeling and simulation can play a fundamental role. From a scientific perspective, it can contribute to understanding the underlying membrane phenomena. In membrane engineering, when combined with the modeling of other units, simulation supports process design and development, allowing performance optimization and enabling efficient process control. While many other separation processes are often described using equilibrium-based models, membrane systems are inherently rate-based. Membrane modeling requires accounting for complex interactions among membrane material properties, transport mechanisms, hydrodynamics, and operating conditions. In addition, physicochemical processes such as membrane fouling and scaling must be considered for long-term applications. However, the modularity of membrane systems facilitates scaling and integration into larger processes, thereby enabling more manageable simulation.

Process simulators, except in some specific cases, still include limited or simplified membrane unit models. The main reason lies in the complex interactions described above, which make membrane separations highly case-specific. Membrane researchers, therefore, require a thorough understanding of the underlying phenomena in order to develop reliable membrane models. In addition, they must possess solid mathematical skills and design appropriate experiments to obtain model parameters from experimental data.

Consequently, several modeling levels are typically considered. At the first level, modeling focuses on membrane materials and transport at the microscopic scale. Transport and mechanistic models (e.g., solution–diffusion, Donnan–Steric Pore Model (DSPM), and dusty–gas) as well as phenomenological and empirical models (e.g., resistance-in-series, scaling, and deposition models) are commonly used [4]. These models are usually developed through experiments with small membrane samples or through microscale simulations such as molecular dynamics or pore-network modeling.

A second level of modeling accounts for hydrodynamic effects at the membrane module scale, including phenomena such as concentration polarization and axial dispersion.

These effects are typically investigated at pilot-plant scale and are increasingly supported by computational fluid dynamics (CFD) [5,6].

At a larger scale, system-level modeling integrates complete processes and plants. At this level, simulation is commonly used for process design and optimization, as well as for integrating membrane units into hybrid systems with other unit operations, such as adsorption, reaction, or distillation [7–9].

Programming and well-established numerical algorithms continue to play an important role in solving and exploiting model results. However, new Artificial Intelligence techniques are emerging as a complementary approach. These techniques include artificial neural networks, machine learning methods, genetic algorithms, and data-driven surrogate models [10,11].

Although the benefits of modeling and simulation in membrane science are considerable, simulation results must always be critically assessed against experimental observations, and the effects of uncertainty should be carefully evaluated [12–14].

2. Overview of Published Articles

This Special Issue includes contributions that address several aspects of modeling and simulation in membrane science and engineering, as discussed in the Introduction. The contributions have been arranged following a progressive thematic logic from fundamental materials, modeling methods, process applications, to integrated systems:

- I. Membrane Materials and Transport Mechanisms (contributions (1)–(3));
- II. Physicochemical Phenomena Affecting Membrane Performance (contribution (4));
- III. Data-Driven Modeling and Artificial Intelligence (contributions (5), (6));
- IV. Filtration Process Modeling and Optimization (contributions (7), (8));
- V. Desalination and Industrial Membrane Systems (contributions (9)–(11));
- VI. Biological Membrane Systems (contribution (12));
- VII. Energy Perspective (contribution (13)).

We start with three fundamental studies on membrane structure and transport, which provide a basis for membrane modeling in their respective fields. Contribution (1) investigates the relationship between polymer structure and gas separation performance in poly(arylene ether ketone)s and poly(diphenylene phthalide) membranes. The study provides valuable insights into how polymer molecular architecture influences permeability and selectivity. The work (2) studies hydrogen permeation through palladium membranes. Permeation is analyzed through a combined experimental and theoretical evaluation of Sievert's law assumptions, providing an improved understanding of hydrogen transport modeling and explaining differences in experimental observations of the Sievert's exponent. Contribution (3) investigates phenomena in porous media, analyzing the influence of grain membrane geometry on permeability properties in porous stone. It can provide a reference for different grain structures.

Physicochemical phenomena influencing membrane operation are addressed in contribution (4), through the case of reverse osmosis scaling. In this work, calcium carbonate crystallization was investigated using fluorescent-tagged antiscalants. This idea offers a unique opportunity to track the location of scale-inhibitor molecules during calcite scale formation.

The increasing availability of computational tools has led to the development of new modeling approaches based on Artificial Intelligence and on data-driven methods. The potential of applying Artificial Intelligence methods is exemplified in contribution (5). In this work, different control strategies are compared for a peristaltically pumped low-pressure membrane process, demonstrating the potential of advanced control algorithms to improve operational stability in membrane systems. The ideas generated can be used

in a batch process to adjust pressure and crossflow velocity to minimize energy required for the concentration stage or to jointly optimize the operation and cleaning phases. In contribution (6), machine learning techniques are used to analyze the factors influencing the gas-separation performance of carbon molecular sieve membranes. The work results highlight the importance of structural characteristics in gas permeability.

The following contributions shift to unit-operation-scale studies focusing on filtration processes and performance optimization. Gas sparging-assisted microfiltration of bacterial cultivation broths is modeled and optimized using response surface methodology and genetic algorithms in (7), while a related study (8) investigated the use of Kenics static mixers combined with gas sparging to enhance crossflow microfiltration performance and mitigate membrane fouling.

Next, contributions expand to system-level simulations of integrated membrane processes for desalination and environmental applications. A hybrid multi-stage flash–reverse osmosis desalination system is modeled and structurally optimized in (9) to improve system performance. The work provides detailed model-based numerical calculations useful for design. In the work (10), modeling and operational optimization were applied to reverse osmosis for treating wastewater from coal-fired power plants. The work is a significant effort in the development of zero-emission wastewater treatment systems. Another system-level study (11) examines atmospheric water generation via reverse osmosis technology under different flow configurations. The work determined the reverse osmosis membrane configuration that required lower energy demand and stages.

Contribution (12) is the representative of hybrid biological membrane systems in this Special Issue. Microbial metabolic processes in a hydrogen-based membrane biofilm reactor are modeled to evaluate simultaneous bromate and nitrate reduction, highlighting the importance of coupling biological and transport phenomena in environmental treatment systems.

Finally, a comprehensive review of renewable hydrogen production technologies is presented in (13). The review discusses the main production methods, scale-up challenges, and the role of hydrogen in future energy systems, providing a broader context for membrane-based technologies increasingly employed in hydrogen purification and separation processes. This review has received more than 325 citations at the time of the publication of this Special Issue.

3. Conclusions

Overall, the contributions to this Special Issue are representative examples of the main modeling approaches used in membrane science and engineering. From fundamental material studies to process simulation and optimization, these works demonstrate how these techniques can contribute to the development and performance optimization of membrane technologies. To date, the average number of citations of the contributions to this Special Issue is higher than the journal average, indicating strong interest in membrane modeling and simulation and highlighting the quality and impact of the published works.

These developments suggest that modeling, simulation, and data-driven methods will continue to play a central role in the future advancement and industrial implementation of membrane technologies.

Funding: This research received no external funding.

Acknowledgments: As Guest Editor of the Special Issue “Modeling and Simulation of Industrial and Environmental Processes with Membranes”, I express my deep appreciation to all authors whose valuable work was published under this issue.

Conflicts of Interest: The author declares no conflicts of interest.

List of Contributions:

- Alentiev, A.; Chirkov, S.; Nikiforov, R.; Buzin, M.; Miloserdov, O.; Ryzhikh, V.; Belov, N.; Shaposhnikova, V.; Salazkin, S. Structure–Property Relationship on the Example of Gas Separation Characteristics of Poly(Arylene Ether Ketone)s and Poly(Diphenylene Phtalide). *Membranes* **2021**, *11*, 677. <https://doi.org/10.3390/membranes11090677>.
- Alraeesi, A.; Gardner, T. Assessment of Sieverts Law Assumptions and ‘n’ Values in Palladium Membranes: Experimental and Theoretical Analyses. *Membranes* **2021**, *11*, 778. <https://doi.org/10.3390/membranes11100778>.
- Shi, R.; Xiao, H.; Shao, C.; Huang, M.; He, L. Study on the Influence of Geometric Characteristics of Grain Membranes on Permeability Properties in Porous Sandstone. *Membranes* **2021**, *11*, 587. <https://doi.org/10.3390/membranes11080587>.
- Popov, K.; Oshchepkov, M.; Pervov, A.; Golovesov, V.; Ryabova, A.; Trukhina, M.; Tkachenko, S. A Case Study of Calcium Carbonate Crystallization during Reverse Osmosis Water Desalination in Presence of Novel Fluorescent-Tagged Antiscalants. *Membranes* **2022**, *12*, 194. <https://doi.org/10.3390/membranes12020194>.
- Díez, J.L.; Masip-Moret, V.; Santafé-Moros, A.; Gozávez-Zafrilla, J.M. Comparison of Artificial Intelligence Control Strategies for a Peristaltically Pumped Low-Pressure Driven Membrane Process. *Membranes* **2022**, *12*, 883. <https://doi.org/10.3390/membranes12090883>.
- Pan, Y.; He, L.; Ren, Y.; Wang, W.; Wang, T. Analysis of Influencing Factors on the Gas Separation Performance of Carbon Molecular Sieve Membrane Using Machine Learning Technique. *Membranes* **2022**, *12*, 100. <https://doi.org/10.3390/membranes12010100>.
- Jokić, A.; Pajčin, I.; Lukić, N.; Vlajkov, V.; Kiralj, A.; Dmitrović, S.; Grahovac, J. Modeling and Optimization of Gas Sparging-Assisted Bacterial Cultivation Broth Microfiltration by Response Surface Methodology and Genetic Algorithm. *Membranes* **2021**, *11*, 681. <https://doi.org/10.3390/membranes11090681>.
- Jokić, A.; Lukić, N.; Pajčin, I.; Vlajkov, V.; Dmitrović, S.; Grahovac, J. Kenics Static Mixer Combined with Gas Sparging for the Improvement of Cross-Flow Microfiltration: Modeling and Optimization. *Membranes* **2022**, *12*, 690. <https://doi.org/10.3390/membranes12070690>.
- He, L.; Jiang, A.; Huang, Q.; Zhao, Y.; Li, C.; Wang, J.; Xia, Y. Modeling and Structural Optimization of MSF-RO Desalination System. *Membranes* **2022**, *12*, 545. <https://doi.org/10.3390/membranes12060545>.
- He, L.; Xia, Y.; Li, C.; Jiang, A.; Zhao, Y.; Xie, F. Simulation and Operational Optimization of RO-Based Desalination for Coal-Fired Power Plants’ Wastewater. *Membranes* **2022**, *12*, 478. <https://doi.org/10.3390/membranes12050478>.
- Fill, M.; Kleingries, M. Modeling and Simulation of Either Co-Current or Countercurrent Operated Reverse-Osmosis-Based Air Water Generator. *Membranes* **2021**, *11*, 913. <https://doi.org/10.3390/membranes11120913>.
- Jiang, M.; Zhang, Y.; Zhang, J.; Dai, X.; Li, H.; Zhang, X.; Wu, Z.; Zheng, J. Model Evaluation of the Microbial Metabolic Processes in a Hydrogen-Based Membrane Biofilm Reactor for Simultaneous Bromate and Nitrate Reduction. *Membranes* **2022**, *12*, 774. <https://doi.org/10.3390/membranes12080774>.
- Agyekum, E.B.; Nutakor, C.; Agwa, A.M.; Kamel, S. A Critical Review of Renewable Hydrogen Production Methods: Factors Affecting Their Scale-Up and Its Role in Future Energy Generation. *Membranes* **2022**, *12*, 173. <https://doi.org/10.3390/membranes12020173>.

References

- Baker, R.W. *Membrane Technology and Applications*; John Wiley & Sons: Hoboken, NJ, USA, 2007.
- Purkait, M.K.; Singh, R. *Membrane Technology in Separation Science*; CRC Press: Boca Raton, FL, USA; Taylor & Francis: Abingdon, UK, 2018.
- Rezazazemi, M.; Younas, M. *Membrane Contactor Technology: Water Treatment, Food Processing, Gas Separation, and Carbon Capture*; Wiley-VCH: Weinheim, Germany, 2022.
- Roy, A.; Moulik, S.; Kamesh, R.; Mullick, A. *Modeling in Membranes and Membrane-Based Processes*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2020.

5. Imran, M.; Lau, K.K.; Ahmad, F.; Mohd Laziz, A. A Comprehensive Review of Computational Fluid Dynamics (CFD) Modelling of Membrane Gas Separation Process. *Results Eng.* **2025**, *26*, 105531. [CrossRef]
6. Sablani, S.; Goosen, M.; Al-Belushi, R.; Wilf, M. Concentration Polarization in Ultrafiltration and Reverse Osmosis: A Critical Review. *Desalination* **2001**, *141*, 269–289. [CrossRef]
7. Kim, J.; Wu, B.; Jeong, S.; Jeong, S.; Kim, M. Recent Advances of Membrane-Based Hybrid Membrane Bioreactors for Wastewater Reclamation. *Front. Membr. Sci. Technol.* **2024**, *3*, 1361433. [CrossRef]
8. Davoodbeygi, Y.; Askari, M.; Salehi, E.; Kheirieh, S. A Review on Hybrid Membrane-Adsorption Systems for Intensified Water and Wastewater Treatment: Process Configurations, Separation Targets, and Materials Applied. *J. Environ. Manag.* **2023**, *335*, 117577. [CrossRef] [PubMed]
9. Ang, W.L.; Mohammad, A.W.; Hilal, N.; Leo, C.P. A Review on the Applicability of Integrated/Hybrid Membrane Processes in Water Treatment and Desalination Plants. *Desalination* **2015**, *363*, 2–18. [CrossRef]
10. Venkatasubramanian, V. The Promise of Artificial Intelligence in Chemical Engineering: Is It Here, Finally? *AIChE J.* **2019**, *65*, 466–478. [CrossRef]
11. Ignacz, G.; Bader, L.; Beke, A.K.; Ghunaim, Y.; Shastry, T.; Vovusha, H.; Carbone, M.R.; Ghanem, B.; Szekely, G. Machine Learning for the Advancement of Membrane Science and Technology: A Critical Review. *J. Membr. Sci.* **2025**, *713*, 123256. [CrossRef]
12. Monroe, J.I.; Thamaraiselvan, C.; Wickramasinghe, S.R. Grand Challenges in Membrane Transport, Modeling and Simulation. *Front. Membr. Sci. Technol.* **2024**, *2*, 1357625. [CrossRef]
13. Sarrazin, F.; Pianosi, F.; Wagener, T. Global Sensitivity Analysis of Environmental Models: Convergence and Validation. *Environ. Model. Softw.* **2016**, *79*, 135–152. [CrossRef]
14. Gozávez-Zafrilla, J.M.; Santafé-Moros, A. Uncertainty and Global Sensitivity Analysis of a Membrane Biogas Upgrading Process Using the COCO Simulator. *ChemEngineering* **2025**, *9*, 94. [CrossRef]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.



Article

Structure-Property Relationship on the Example of Gas Separation Characteristics of Poly(Arylene Ether Ketone)s and Poly(Diphenylene Phtalide)

Alexandre Alentiev ^{1,*}, Sergey Chirkov ¹, Roman Nikiforov ¹, Mikhail Buzin ², Oleg Miloserdov ³, Victoria Ryzhikh ¹, Nikolay Belov ¹, Vera Shaposhnikova ² and Sergey Salazkin ²

¹ A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences (TIPS RAS), 119991 Moscow, Russia; sm1th@ips.ac.ru (S.C.); nru@ips.ac.ru (R.N.); kochenkova@ips.ac.ru (V.R.); belov@ips.ac.ru (N.B.)

² A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences (INEOS RAS), 119334 Moscow, Russia; buzin@ineos.ac.ru (M.B.); vsh@ineos.ac.ru (V.S.); sns@ineos.ac.ru (S.S.)

³ V.A. Trapeznikov Institute of Control Sciences, Russian Academy of Sciences (ICS RAS), 117997 Moscow, Russia; oleg_milos@mail.ru

* Correspondence: alentiev@ips.ac.ru; Tel.: +7-916-201-68-55

Abstract: Three poly(arylene ether ketone)s (PAEKs) with propylidene (C1, C2) and phtalide (C3) fragments, and one phtalide-containing polyarylene (C4), were synthesized. Their chemical structures were confirmed via ¹H NMR, ¹³C NMR and ¹⁹F NMR spectroscopy. The polymers have shown a high glass transition temperature (>155 °C), excellent film-forming properties, and a high free volume for this polymer type. The influence of various functional groups in the structure of PAEKs was evaluated. Expectedly, due to higher free volume the introduction of hexafluoropropylidene group to PAEK resulted in higher increase of gas permeability in comparison with propylidene group. The substitution of the fluorine-containing group on a rigid phtalide moiety (C3) significantly increases glass transition temperature of the polymer while gas permeation slightly decreases. Finally, the removal of two ether groups from PAEK structure (C4) leads to a rigid polymer chain that is characterized by highest free volume, gas permeability and diffusion coefficients among the PAEKs under investigation. Methods of modified atomic (MAC) and bond (BC) contributions were applied to estimate gas permeation and diffusion. Both techniques showed reasonable predicted parameters for three polymers while a significant underestimation of gas transport parameters was observed for C4. Gas solubility coefficients for PAEKs were forecasted by “Short polymer chain surface based pre-diction” (SPCSBP) method. Results for all three prediction methods were compared with the ex-perimental data obtained in this work. Predicted parameters were in good agreement with ex-perimental data for phtalide-containing polymers (C3 and C4) while for propylidene-containing poly(arylene ether ketone)s they were overestimated due to a possible influence of propylidene fragment on indices of oligomeric chains. MAC and BC methods demonstrated better prediction power than SPCSBP method.

Keywords: polyether ketones; polymer synthesis; gas separation membranes; permeability; diffusion; properties prediction

1. Introduction

Over the past twenty years, the separation of gas mixtures has been one of the most rapidly developing and knowledge-intensive areas of membrane technology. The following different types of materials are used to prepare membranes for gas separation: polymeric materials, such as homo- and copolymers [1]; inorganic materials, such as carbon molecular sieves [2] or metals [3]; and polymer matrices filled with inorganic particles, such as so-called mixed-matrix membranes [4]. In the majority of membrane

gas separation processes, asymmetric or composite polymer membranes are used, the materials of the thin selective layer [5] of which, as a rule, are glassy amorphous polymers.

Mass transfer in such membranes is carried out by the solution-diffusion mechanism. The stationary gas flow through the membrane is directly proportional to the pressure drop and inversely proportional to the thickness of the membrane. In this case, the proportionality coefficient is the gas permeability coefficient (P) for the material of the selective membrane layer. In the literature, P is usually expressed in off-system units, i.e., Barrer ($1 \text{ Barrer} = 10^{-10} \text{ cm}^3(\text{STP}) \text{ cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$). The P values for polymer materials vary within 3–8 orders of magnitude, depending on the nature of the polymer and the gas [5,6]. P for the polymer–gas system is determined by the gas diffusion coefficient D and gas solubility coefficient S of the material [6], as follows:

$$P = D \cdot S, \quad (1)$$

In the literature on the membrane topic, as a rule, D is expressed in $\text{cm}^2 \text{ s}^{-1}$, and S is expressed in $\text{cm}^3(\text{STP}) \text{ cm}^{-3} \cdot \text{cmHg}^{-1}$ or in $\text{cm}^3(\text{STP}) \text{ cm}^{-3} \cdot \text{atm}^{-1}$.

An important factor characterizing the efficiency of the gas separation process is the ideal selectivity of the separation of i and j gases, as follows:

$$\alpha_{ij} = P_i/P_j, \quad (2)$$

The potential efficiency of the material for gas separation is determined by the position of the experimentally measured values P and α for the polymer on the permeability–selectivity diagrams (Robeson diagrams), relative to the empirical so-called “upper bounds” [7,8] of the overall distribution. The “upper bounds” on the Robeson diagrams are formed by polymers with the most-favorable combination of permeability and selectivity. The coefficients of permeability, diffusion, and solubility, as well as the ideal selectivity of gas separation, are considered to be the transport parameters of the polymer–gas system, at a constant temperature. To separate mixtures of non-condensable gases, such as H_2 , He , N_2 , O_2 , CO_2 , and CH_4 , glassy amorphous polymers with high diffusion selectivity are used as materials for the selective layer [6,9].

The chemical structure of a polymer affects its macroscopic properties in a complex way. Firstly, it is connected to the intermolecular interactions in the polymer and its chain rigidity. These properties subsequently determine the glass transition temperature, density, free volume, and other macroscopic characteristics of the polymer [6,10]. Moreover, the latter, in turn, have an influence on the gas transport properties. Thus, most of the works on the design of the chemical structure of polymers are based on the assumption that a higher fractional free volume (and lower density) leads to higher gas permeability, while free volume distribution and also intermolecular interactions have an effect on the selectivity of different gas pairs [6]. For a long time, the main direction to improve gas transport characteristics consisted of an introduction of bulky moieties into a polymer structure [11]. However, the latest trends in high-performance polymer preparations include the structures with “kink” fragments, e.g., PIMs, polymers with a bisfluorene fragment, Tröger base polymers, and iptycene-containing polymers [12–14]. Thus, phthalide-containing polymers seem relevant for the study of such structures.

The extensive information accumulated to date on the transport parameters of polymers with different chemical structures of the elementary unit [15,16], allows one to not only search for empirical relationships between the chemical structure of the elementary unit with the transport characteristics of polymers [7,8,13,17–28], but also to predict transport parameters from the chemical structure of the elementary unit [29]. Such predictions are possible both by the group contribution methods [29–39], but also by using elements of the graph theory [29,40–42] and geometrical indices [43,44], as well as by using neural networks [29,45,46] or computer modeling [29,47–56]. Computer modeling by molecular dynamics, or Monte Carlo [50,55,56], is a fast-developing method for predicting the transport parameters of polymers, and, from the point of view of

the physical nature of the process, the most adequate one. However, these methods take a lot of time for calculations on supercomputers and, with all the prospects, they cannot currently be used for a wide range of polymers, although they seem necessary for modeling local tasks for specific polymer materials. The use of self-learning neural networks to predict the properties of substances requires large datasets (several tens of thousands of structures studied), which is unreachable for the transport parameters of polymers; currently, no more than 2000 structures have been studied. Therefore, the use of neural networks for the adequate prediction of the transport parameters of polymers is currently limited. More attractive for the existing datasets [15,16] are the various variants of the group contribution method that was used for these datasets before [29,35,36,38], or the developed methods of geometrical indices [43,44], which takes into account the geometric parameters of the model fragments of polymer chains. However, when using any prediction methods, it is necessary to verify these methods for new polymers that were not included in the dataset, on the basis of which these contributions or indices were determined.

Among the classes of polymers presented in the database [15], not all are equally present. Polyimides have the most numerous representation (Table 1); therefore, for this class, the predicted data are closest to the experimental ones [29,32,35]. For such a practically important and extensive class of polymers as poly(arylene ether ketone)s [57, 58], the database [15] contains only 41 different structures, so for this class, the verification of predicted data is very interesting.

Table 1. Distribution of polymers throughout classes.

Class	Number of Polymers
Polyimides	394
Polyacetylenes	107
Polyesters	88
Copolymers	81
Polyethers	72
Polynorbornenes (metathesis and additive)	70
Polysulfones	52
Polyamidoimides	40
Polyamides	37
Other nitrogen-containing polymers	31
Polystyrenes	22
Polycarbonates	19
Vinyl polymers	15
Polyacrylates	15
Other carbon-chain polymers	10
Other hetero-chain polymers	8
Polyphosphazenes	4

Thus, in this work, a number of poly(arylene ether ketone)s (PAEKs), as well as poly(diphenylene phthalide), which only has a common structural element with one of the PAEKs, were synthesized and studied, and the process of verifying various methods for predicting transport parameters for these polymers was carried out.

2. Materials and Methods

2.1. Polymer Synthesis

The synthesis of poly(arylene ether ketone)s (PAEKs: C1–C3, Figure 1) was carried out by polycondensation method according to the mechanism of the reaction of nucleophilic substitution of activated halogen in arylene dihalide, by the interaction of 4,4'-difluorobenzophenone with dipotassium phenolates of bisphenols (bisphenol A, bisphenol AF, phenolphthalein), similar to the method described in [59] (Figure 1). Further, 4,4'-Difluorobenzophenone (0.0988 mol), bi-sphenol(2,2-bis(4'-hydroxyphenyl)propane

or 2,2-bis(4'-hydroxyphenyl)hexafluoropropane or 3,3-bis(4'-hydroxyphenyl) phthalide) (0.1 mol), 4-fluorobenzophenone (0.0024 mol), pre-milled freshly calcined K₂CO₃ (0.13 mol), N,N-dimethylacetamide (200 mL), and chlorobenzene (100 mL) were loaded in an argon-blown four-necked flask equipped with a stirrer, an argon supply tube, and a system for azeotropic removal of water. The flask was heated on an oil bath whose temperature was increased within ~0.5 h up to 185 °C. The time of synthesis after complete removal of an azeotropic chlorobenzene–water mixture was 7 h. The reaction mixture was cooled and dissolved in chloroform. The resulting solution was filtered from salts and washed with stirring many times with water. After evaporation of the chloroform solution at 25 °C and drying for 18 h with a gradual increase in the temperature from 60 to 140 °C, and then for 25 h at 160 °C. The PAEKs was obtained as a film in yield of 99%; the reduced viscosities (η_{red}) were 0.62 dL/g (for C1), 0.53 dL/g (for C2) and 0.78 dL/g (for C3).

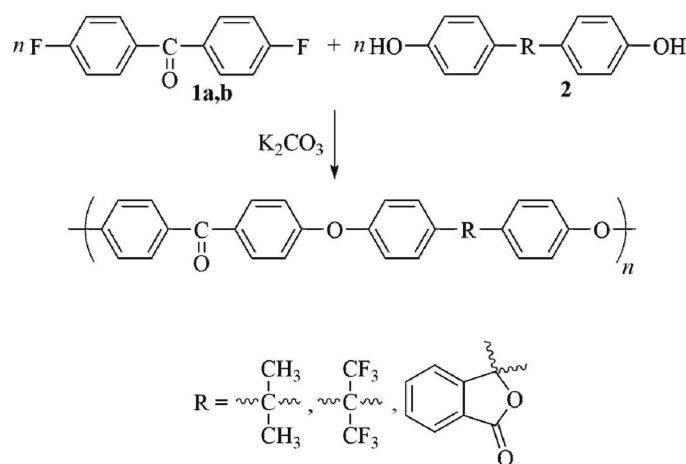


Figure 1. PAEKs C1–C3 synthesis scheme.

Reduced viscosity η_{red} was determined in chloroform at 25 °C and a polymer concentration of 0.5 g for 100 mL of a solvent, using an Ubbelohde viscometer with a capillary diameter of 0.6 mm. The synthesis of polydiphenylene phthalide was carried out by the following scheme [60] (Figure 2).



Figure 2. Poly(diphenylene phthalide) C4 synthesis scheme.

The three-necked flask (50 cm³) equipped with a stirrer, a gas-inlet tube and air condenser with bubble counter was purged with argon. Then 2'-carboxy-4-phenylbenzophenone acid pseudo chloride (10 g) and nitrobenzene (15 mL), which was purified by vacuum distillation and dried over molecular sieves, were placed into the flask. The solution obtained was heated in inert atmosphere to 80 °C (in bath) and then 0.4 mL of SbCl₅ (it was synthesized by chlorination of SbCl₃ and purified by vacuum distillation) was added. Polycondensation was carried out at 80 °C for 30 h and then at 100 °C for 10 h.

After completion of synthesis and cooling of reaction mixture, polymer was dissolved in 300 mL of purified chloroform. Polymer solution was filtered and the polymer was precipitated at stirring and slow adding in methanol (near 1000 mL of methanol purified by distillation). The precipitate obtained was filtered and washed with methanol. Then repeated extractions by methanol and acetone (methanol and acetone were purified by distillation) were performed. The polymer was dried at 120 °C. The polymer yield was

8.2 g. Polymer reduced viscosity was 0.56 dL/g at 25 °C (0.5 g of polymer per 100 mL of the chloroform).

2.2. Polymer NMR Characterization

Chemical structures of C1–C4 polymers were confirmed using ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra. Spectra for C1 and C3 were previously reported in [61], spectra for C4 were previously reported in [62].

The ^1H and ^{13}C NMR spectra of C1–C3 samples were measured on an Avance 400 Bruker spectrometer (400.13 and 100.61 MHz, respectively) using CDCl_3 solutions; Me_4Si was used as an internal standard. Signals in the ^1H and ^{13}C NMR spectra were assigned according to the data calculated using program ACDLabs. ^{19}F NMR for C2 sample was recorded on an Avance 300 Bruker spectrometer (282.40 MHz) (Billerica, MA, USA) for solution in CDCl_3 using CF_3COOH as the external standard.

Results of ^1H NMR and ^{13}C NMR analyses are provided in Tables S1 and S2 (Supplementary Materials), respectively.

The ^{19}F NMR spectrum of sample C2 contains a singlet in the region of minus 63.90 ppm, which is characteristic of the chemical shift of the CF_3 group.

2.3. Investigation Methods

Polymer films were obtained by casting on a cellophane support from a 5% solution in chloroform (reagent grade) with drying for 2–3 days at room temperature, followed by bringing it to a constant mass in vacuum.

Differential scanning calorimetry (DSC) studies of the films obtained were performed on a DSC-3 apparatus (Mettler-Toledo, Columbus, OH, USA) equipped with a liquid nitrogen cooling system. Measurements were performed in dry argon with purging through the cell at a gas flow rate of 60 mL/min and at a heating rate of 10 °C/min. The temperature signal was calibrated by the beginning of the melting of indium and zinc at a heating rate of 10 °C/min. The heat flow rate was calibrated considering the melting heat of indium. To assess the presence of residual solvent in films, TGA method in air at a heating rate of 10 °C/min was used (Derivatograph-C apparatus, MOM Budapest, Hungary).

The density of polymer films ρ (in g/cm^3) was determined at room temperature (22 ± 2 °C) by hydrostatic weighing in propanol-2. The fractional free volume (FFV) was determined using the Bondi method [63], as follows:

$$\text{FFV} = 1 - 1.3 \cdot V_w / V_{sp}, \quad (3)$$

where V_w is the van der Waals volume of a monomer unit (cm^3/mol); $V_{sp} = M/\rho$ is the specific occupied volume of a polymer (cm^3/mol); M is the molecular mass of the monomer unit of a polymer (g/mol).

The gas (He , H_2 , O_2 , N_2 , CO_2 , CH_4) permeability (P) and diffusion (D) coefficients at a temperature of (21 ± 2 °C) for the prepared films were obtained by the integral barometric method on the MKS Barotron installation. The software based on “LabVIEW” was used to control the experiment. The experiments were carried out at room temperature; upstream pressure was about 1 atm. In the case of studying the permeability of oxygen, the upstream pressure was varied in range of 1–5 atm, and it was shown that the permeability coefficients of this gas, as well as the diffusion coefficients, remained constant. The downstream pressure did not exceed 1.3×10^{-3} atm; therefore, under the conditions of the experiment, the reverse diffusion of the penetrating gas was neglected. Permeability coefficient P and diffusion coefficient D were determined via the curve of gas permeation through the polymer film into a calibrated volume (P : by the slope of the linear dependence of the flow through a film after the steady-state mass transfer was reached; D : by the method of Daynes-Barrer using the time lag θ (s): $D = l^2/6\theta$, where l is the film thickness). The solubility coefficients (S) were calculated from the experimental values of P and D using the formula $S = P/D$. From the data obtained, ideal separation

selectivities ($\alpha = P_i/P_j$) and diffusion selectivities ($\alpha_D = D_i/D_j$) were found for different i and j gas pairs. The experimental measurement error for P was 5%, for D was 10% and, subsequently, the calculation errors were 15%, 10%, and 20% for S , α and α_D , respectively.

The experimental P and D were extrapolated to 35 °C using the method from [64] in order to perform comparison with the predicted values based on the database [15].

2.4. Prediction Methods

2.4.1. The Method of Modified Atomic Contributions (MAC) and the Method of Bond Contributions (BC)

The methods used in this work to predict gas permeability and diffusion coefficients were described previously [32,38]. Summary is provided below.

A set of polymers is selected from the database [15]. All structures of repeat units are presented as molecular graphs in the database [15]. Structural formula of the repeat unit is then split into a set of fragments (atoms or bonds with the nearest neighbors), and an increment (variable, representing quantitative contribution of the fragment) of a physical property in question is assigned to every fragment. The sum of these increments multiplied by the normalization factor (introduced to consider a difference in polymer-chain molecular weights or lengths) is the predicted value of the physical property being calculated. The system of such equations (Equations (4) and (5) for MAC and BC, respectively) for a set of polymers selected is then solved to get a number of increment values and a number of predicted property values. The increments obtained are then used to calculate a new polymer property. All of the operations described above from the splitting of the polymers from the dataset to the calculation of increments and predicted properties are performed via RIADA software [38]. The difference between the modified atomic contributions (MAC) method and bond contribution (BC) method is in the way of repeat unit splitting into the fragments. In both cases the polymer repeat unit is split into the atoms (MAC) or bonds (BC) of the main chain and side groups; however, BC method also includes the “mixed” bonds connecting main chain with the side groups. The universal scheme for MAC and BC methods is provided in Figure 3.

$$\left\{ \begin{array}{l} \lg X_1 = \sum_i \left(\frac{m_i n_{i1}}{M_1} \cdot I_i \right) \\ \lg X_2 = \sum_i \left(\frac{m_i n_{i2}}{M_2} \cdot I_i \right) \\ \dots \\ \dots \\ \dots \\ \lg X_k = \sum_i \left(\frac{m_i n_{ik}}{M_k} \cdot I_i \right) \end{array} \right. \quad (4)$$

$$\left\{ \begin{array}{l} \lg X_1 = \sum_i \left(\frac{n_{i1}}{N_1} \cdot I_i \right) \\ \lg X_2 = \sum_i \left(\frac{n_{i2}}{N_2} \cdot I_i \right) \\ \dots \\ \dots \\ \dots \\ \lg X_k = \sum_i \left(\frac{n_{ik}}{N_k} \cdot I_i \right) \end{array} \right. \quad (5)$$

where k is number of polymers in test set; i is total number of group types (atoms for MAC or bonds for BC); I is an increment of a given group; X is a physicochemical property tested (permeability or diffusion coefficient); n is number of groups in a given polymer; m is molar mass of atom; M is molar mass of a monomer unit; N is total number of bonds in a monomer unit.

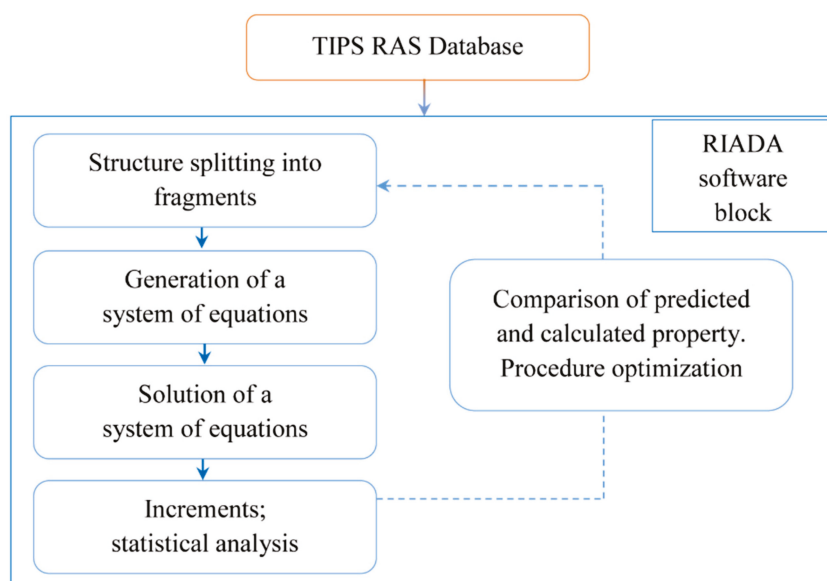


Figure 3. Universal flowchart for group contribution methods (MAC and BC).

2.4.2. Short Polymer Chain Surface-Based Prediction

This paper continues the development of practical application of the quantitative structure–property relationships (QSPR)-based short polymer chain surface-based prediction (SPCSBP) method from [43,44,65]. The method consists of modeling of the polymer macromolecule conformations with a size of about several hundred atoms. The approach is to calculate the accessible surface areas of the spherical model of a molecule using the Lee-Richards algorithm [66] for a large set of conformations of individual polymer chains and in constructing the dependencies of the accessible surface area (ASA) from the probe radius (Figure 4) on their basis. The coefficients of linear approximation of the obtained dependencies are used as explanatory variables in multiple linear regression. The significant variables and their weights in the regression are found based on experimental measurements from the database of the A.V. Topchiev Institute of Petrochemical Synthesis of the Russian Academy of Sciences [15], obtained either by direct S measurements or by division of experimental permeability coefficients by experimental diffusion coefficients ($S = P/D$).

Conformations of polymer chains are the result of molecular mechanical modeling, the procedure of which is implemented in the RDKit (Python) environment. The developed SPCSBP method is performed using freely distributed software, is maximally automated, has the possibility of parallelization on a cluster and has an acceptable calculation time for single polymer. The method also ensures the stability of the obtained results and their reproducibility, and is applicable for specific polymers used in membrane gas separation.

Schematic flowchart of the method is provided in Figure 4 below.

Mean absolute percentage errors (MAPEs) (Equation (6)) and mean percentage errors (MPEs) (Equation (7)) were calculated for all of the prediction methods used in order to assess these methods accuracies and compare them, as follows:

$$MAPE = \frac{100\%}{n} \sum_{i=1}^n \left| \frac{A_t - F_t}{A_t} \right|, \quad (6)$$

$$MPE = \frac{100\%}{n} \sum_{i=1}^n \left| \frac{A_t - F_t}{A_t} \right| \quad (7)$$

where A_t is the actual value, F_t is the forecast value and n is the number of data points.

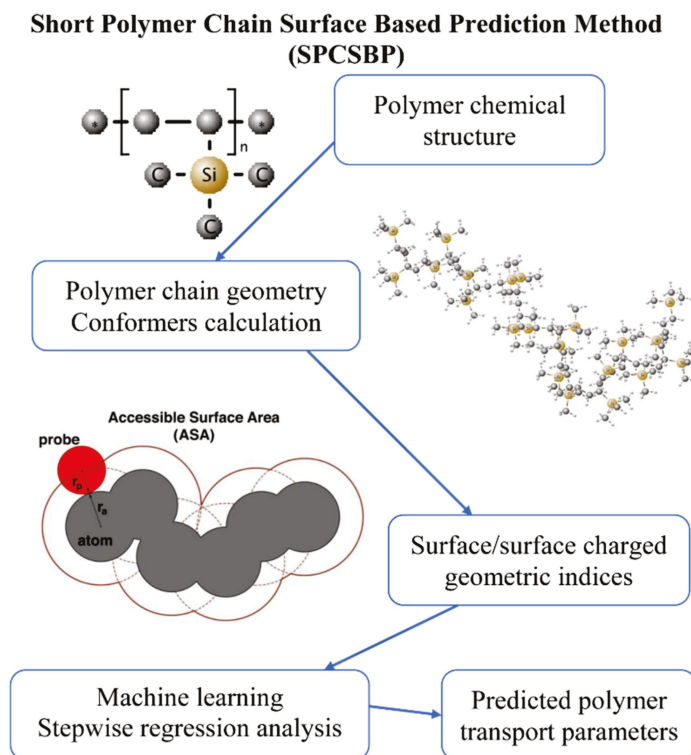


Figure 4. SPCSBP method flowchart.

3. Results and Discussion

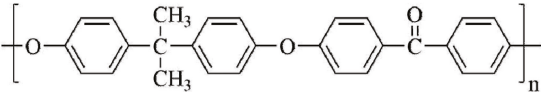
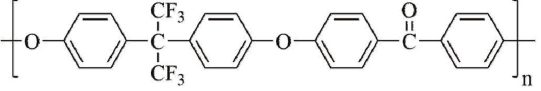
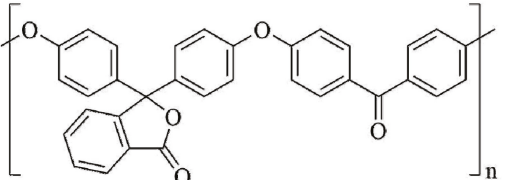
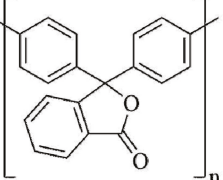
3.1. Thermal Properties and Free Volume

All the polymers synthesized in the work have high glass transition temperatures (T_g) (Table 2). The T_g for poly(diphenylene phthalide) C4 is not detected and, apparently, it is higher than the decomposition temperature ($>440\text{ }^\circ\text{C}$). At the same time, according to thermomechanical analysis (TMA) data [67], a softening temperature of $420\text{ }^\circ\text{C}$ is observed for this polymer. Poly(diphenylene phthalide) C4, in fact, is a fragment of poly(arylene ether ketone) C3, without the $-\text{O}-\text{Ph}-(\text{C}=\text{O})-\text{Ph}-\text{O}-$ group; therefore, in a number of synthesized polyheteroarylenes, it is interesting to trace not only the influence of substituents in the main chain, but also the change in its nature. Thus, the traditional replacement of $-\text{C}(\text{CH}_3)_2-$ (C1) with a more voluminous fluorine-containing group, $-\text{C}(\text{CF}_3)_2-$ (C2), leads to an increase in FFV and T_g (Table 2). It is obvious that the presence of trifluoromethyl groups in the structure of the polymer C2 should reduce the interchain interactions [68] in the polymer, compared to C1, and, subsequently, reduce the T_g . However, this effect is inferior to the influence of the chain stiffness, which ultimately causes a slight increase in the glass transition temperature for the polymer C2.

The introduction of a rigid and polar phthalide group (C3) into the main chain of PAEK also leads to an increase in FFV compared to C1, approaching that for C2 (Table 2). The presence of a polar group should increase the interchain interactions in the C3 polymer, hindering molecular mobility, and thereby causing an increase in the glass transition temperature. Therefore, a significant increase in T_g for the C3 polymer, compared to the glass transition temperatures for C1 and C2, seems reasonable (Table 2).

The exclusion of the PAEK $-\text{O}-\text{Ph}-(\text{C}=\text{O})-\text{Ph}-\text{O}-$ group from the main chain is the reason for a significant increase in the chain stiffness; therefore, despite the polarity of the phthalide group, the free volume of the polymer C4 increases significantly. Thereby, the free volume of the polymers increases in the following series: $\text{C1} < \text{C3} < \text{C2} < \text{C4}$.

Table 2. Physicochemical properties of PAEKs.

Polymer Designation	Structure	T _g , °C	ρ, g/cm ³	FFV, %
C1		155	1.195	10.4
C2		163	1.377	11.9
C3		229 218 [69] 249 [70]	1.259 1.249 [69] -	11.6 12.3 [69] -
C4		>440	1.215	13.3

3.2. Experimental Gas Transport Properties

The experimental gas permeability coefficients for the obtained polymer films are presented in Table 3. As can be observed from Table 3, poly(diphenylene phthalide) C4, which can be attributed to medium-permeability polymers, is characterized by the highest P values for all gases. In general, the P values for all gases change in the same manner as the free volume, and naturally increase in the following series: C1 < C3 < C2 < C4.

Table 3. Experimental gas permeability coefficients P (Barrer¹) for synthesized polymers at (21 ± 2 °C).

Polymer	He	H ₂	O ₂	N ₂	CO ₂	CH ₄
C1	6.8	7.0	0.53	0.068	2.7	0.065
C2	14	11	1.3	0.21	6.7	0.22
C3	8.9	9.7	0.86	0.12	5.0	0.11
C4	32	52	10	2.2	83	2.8

¹ Barrer = 10^{−10} cm³(STP)·cm·cm^{−2}·s^{−1}·cmHg^{−1}.

Slightly different patterns are observed for the gas diffusion coefficients in the synthesized polymers (Table 4). Poly(diphenylene phthalide) C4 is characterized by the highest values of D, in accordance with the value of fractional free volume. The diffusion coefficients for O₂, N₂, CO₂, and CH₄ of C2 are 2.3–3 times less, of C1 are 6–10 times less, and of C3 are 7–12 times less than that of C4. For penetrants with a small molecule size, the differences in the diffusion coefficients are significantly smaller. So, the value of D(H₂) for C2 is only 1.9 times less than that for C4, and for C1 and C3 it is 3 times less. In general, D for all gases increases in the following series: C3 < C1 < C2 < C4. However, it is worth paying attention to the behavior of the gas diffusion coefficients in PAEK C3. When replacing the −C(CF₃)₂− group (C2) with a phthalide moiety (C3), there is a sharp decrease in the diffusion coefficients of permanent gases, by 3–4 times, despite the fact that these polymers have comparable fractional free volumes (Table 4).

Table 4. Experimental gas diffusion coefficients $D \cdot 10^8$ ($\text{cm}^2 \cdot \text{s}^{-1}$) in synthesized polymers at $(21 \pm 2$ °C).

Polymer	He	H ₂	O ₂	N ₂	CO ₂	CH ₄
C1	290	76	1.5	0.41	0.38	0.067
C2	290	120	3.8	1.0	1.2	0.23
C3	230	74	1.2	0.27	0.35	0.056
C4	360	230	8.9	2.7	3.3	0.68

It should be noted that the gas permeability and diffusion coefficients for the polymer C3 (Tables 3 and 4) are consistent with the literature data [69,70].

Generally, as a polymer class, PAEKs show low levels of permeability and diffusion [15]. The bulk phthalide group can be anticipated to increase in terms of its gas permeability and diffusion coefficients. However, there is a significant difference (approximately one order of magnitude) between the P and D of C3 and C4 polymers (Tables 3 and 4), despite the presence of a phthalide group in both of these structures. This can be attributed to the more-rigid main chain of the C4 polymer, allowing the formation of a kinked structure, which is not the case for the C3 polymer, which contains flexible –O– links. One would expect C4 to show a behavior similar to highly permeable kinked polymers that demonstrate microporosity [12–14]. That is not the case though, due to the high dipole moment of the phthalide group that contributes to the high level of interchain interactions for C4.

The behavior of gas permeability and diffusion coefficients has a corresponding effect on the changes in the solubility coefficient S (Table 5) in a series of synthesized polymers. The largest S values for all gases are observed for the polymer C4. However, unlike the data for P and D, the second place, with slightly lower S values for all gases except helium, is occupied by C3. Moreover, the solubility coefficient of CO₂ for the studied polymers increases in the series C2 < C1 < C3 < C4, while S(N₂) increases in the series C1 < C2 < C3 < C4. The solubility coefficients of H₂, O₂, and CH₄ for C1 and C2 are almost the same, so the value of S for the studied polymers increases in the series C1 ≈ C2 < C3 < C4. For helium, since D is determined with the greatest error, it can only be argued that the solubility coefficient for C4 is greater than that for the others. Basically, this indicates the large size of the free volume element (FVE) in C4 and C3 compared to other polymers, which is probably caused by the presence of a rigid, although polar, phthalide fragment.

Table 5. Experimental gas solubility coefficients $S \cdot 10^3$ ($\text{cm}^3(\text{STP}) \cdot \text{cm}^{-3} \cdot \text{cmHg}^{-1}$) for synthesized polymers at $(21 \pm 2$ °C), calculated as P/D.

Polymer	He	H ₂	O ₂	N ₂	CO ₂	CH ₄
C1	0.23	0.92	3.6	1.6	71	9.7
C2	0.48	0.94	3.4	2.1	56	9.6
C3	0.39	1.3	7.2	4.4	140	20
C4	0.89	2.3	11	8.1	250	41

A qualitative comparison of the gas transport parameters of the studied PAEKs C1–C4 with the results obtained for other polymers from the TIPS RAS database can be made by plotting them on the diffusion coefficient–permeability coefficient and solubility coefficient–permeability coefficient diagrams [25]. Since the most attractive results for PAEKs were obtained for the CO₂/N₂ pair, these diagrams are presented for carbon dioxide (Figure 5a,b) and nitrogen (Figure 5c,d). As can be observed from the presented data (Figure 5a,c), the diffusion coefficients of nitrogen and carbon dioxide naturally increase with the increase in gas permeability. However, while the data points for N₂ are located near the “middle line” (least-squares fit for overall dataset on the $D = f(P)$ diagram) of the general point cloud, $D(\text{CO}_2)$ for polymers are below the “middle line”,

which indicates reduced carbon dioxide diffusion coefficients for the corresponding gas permeability level, especially for the PAEKs C3 and C4. Apparently, this is due to increased interchain interactions in polymers containing a phthalide group.

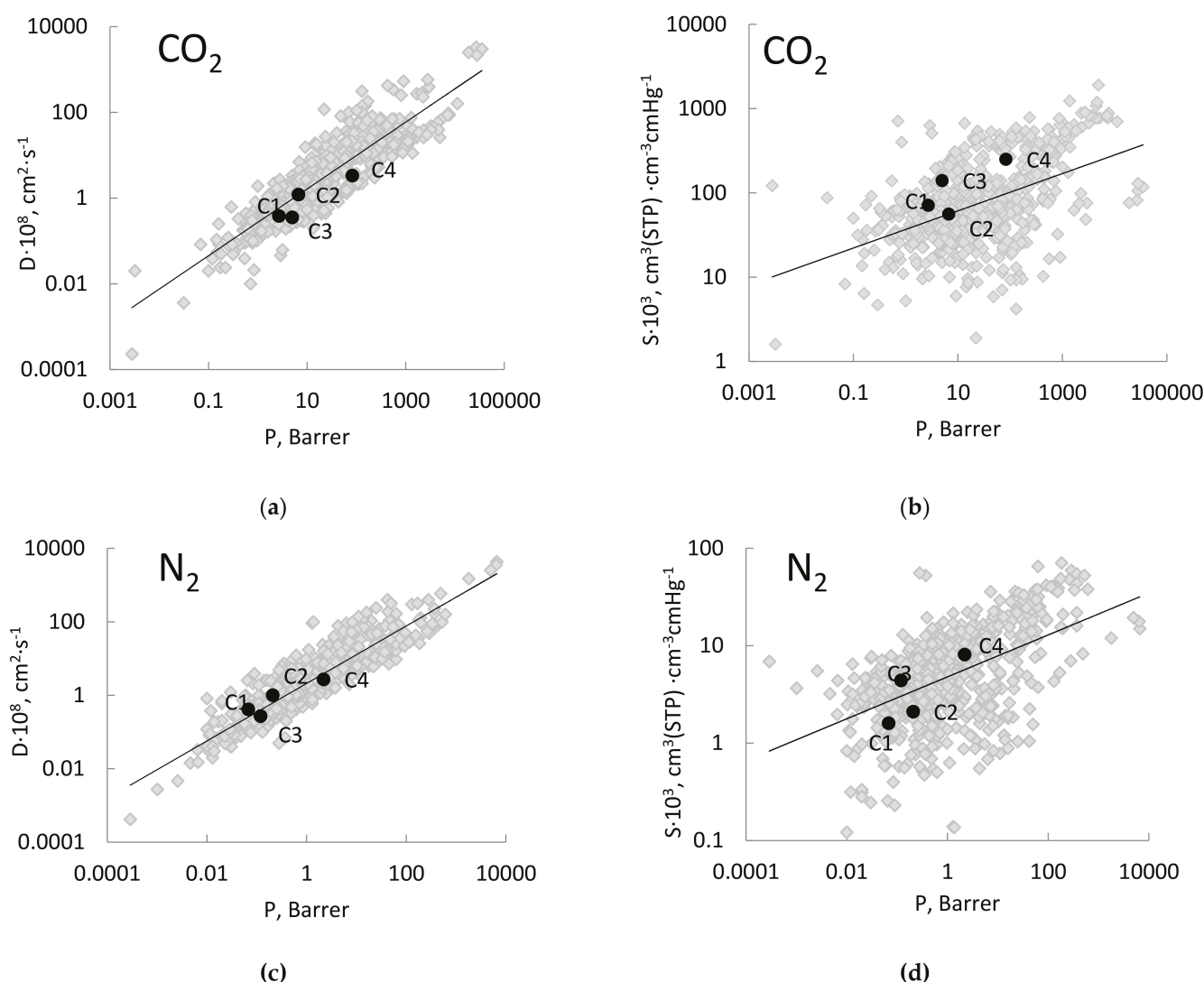


Figure 5. Diagrams of D vs. P and S vs. P for CO₂ (a) and (b), respectively) and N₂ (c) and (d), respectively). The solid black dots correspond to PAEKs C1–C4, the gray dots correspond to P, D and S of the gases for polymers from TIPS database [15].

On similar S vs. P dependencies (Figure 5b,d), the solubility coefficients of N₂ for the polymers C3 and C4 are located above the "middle line", while for polymers with a bisphenol fragment (C1 and C2), they are located below it. Thus, for polymers C3 and C4, the influence of an increased free volume is evident (Table 2). It is noteworthy that the solubility coefficients of carbon dioxide for all the studied polymers lie above the "middle line", with the exception of the polymer with the $-\text{C}(\text{CF}_3)_2-$ group (Figure 5b). This behavior seems to be associated not only with an increased free volume in polymers, but also with the presence of specific interactions of the CO₂ molecule with oxygen-containing phthalide and ketone groups. A similar phenomenon is often recorded when studying sorption and permeability in polymers containing ether groups (e.g., Pebax [71]).

It is worth noting that when replacing the $-\text{C}(\text{CH}_3)_2-$ fragment (C1) with $-\text{C}(\text{CF}_3)_2-$ (C2), despite the increase in the solubility coefficient of N₂ (Figure 5d), there is a significant decrease in $S(\text{CO}_2)$ (Figure 5b), which may indicate a reduced affinity of the polar CO₂ molecule to the fluorine-containing group.

The ideal gas separation selectivities for all the polymers are shown in Table 6; the locations of the studied polymers in the Robeson diagrams for O₂/N₂ and CO₂/N₂ gas pairs are shown in Figure 6a,b, respectively.

Table 6. Different gas pairs ideal selectivities (α) of permeability for synthesized polymers at (21 ± 2 °C).

Polymer	α						
	O ₂ /N ₂	CO ₂ /N ₂	CO ₂ /CH ₄	He/N ₂	H ₂ /CH ₄	He/CH ₄	H ₂ /N ₂
C1	7.9	40	42	100	110	100	100
C2	6.2	32	30	67	50	63	52
C3	7.2	42	45	74	88	81	81
C4	4.5	38	30	15	19	11	24

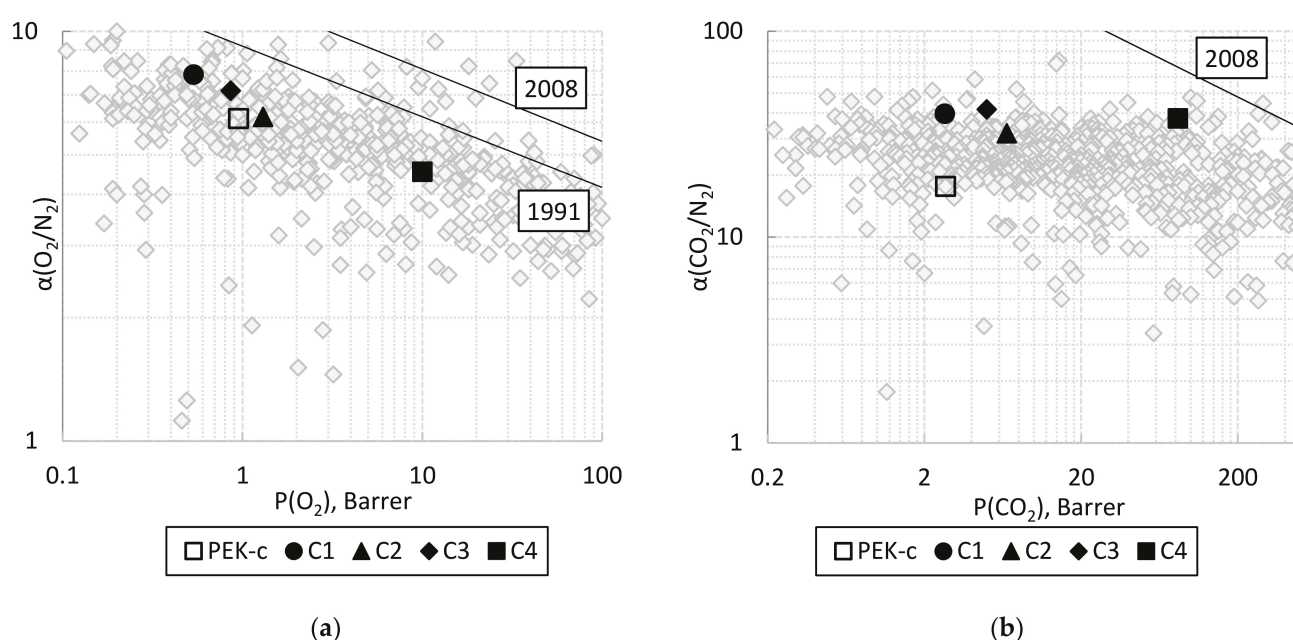


Figure 6. Robeson diagrams for oxygen–nitrogen (a) and carbon dioxide–methane (b) for the studied polymers. For comparison, the data for poly(arylene ether ketone) PEK-c are given [69] (data from [69] are similar to those from [70]). Upper bounds are provided from [7] (1991) and [8] (2008).

As can be observed from Table 6 and Figure 6a, the most permeable C4 has the lowest selectivity for the oxygen–nitrogen gas pair. The selectivity of polymers increases parallel to the upper bound in the diagram, which corresponds to the trade-off effect. In general, the selectivities of the studied polymers are low, with the exception of the CO₂/N₂ pair (Figure 6b). In this diagram, the point for C4 is located near the 2008 upper bound [8] for glassy amorphous polymers. Note that according to the diagrams presented in Figure 5, a high selectivity for the CO₂/N₂ pair for the polymers C1, C3 and C4 should be determined by the increased solubility of carbon dioxide.

3.3. Predicted Gas Transport Parameters

Table 7 present a comparison of the experimental data for the studied polymers extrapolated to 35 °C by the method from [64], and the data predicted by the chemical structure of the elementary unit by the methods of modified atomic contributions and bond contributions [38] at 35 °C.

Table 7. Experimental gas permeability coefficients P (Barrer) for synthesized polymers at 35 °C and predicted data for the same polymers.

Polymer	Type of Data	He	H ₂	O ₂	N ₂	CO ₂	CH ₄	MAPE ¹ , %	MPE ² , %
C1	Experimental	9.33	10.1	0.753	0.120	3.67	0.124	-	-
	MAC	5.3	4.5	0.30	0.037	1.1	0.040	61	61
	BC	7.1	4.9	0.33	0.045	1.3	0.047	53	53
C2	Experimental	17.9	15.0	1.72	0.320	8.16	0.345	-	-
	MAC	28	16	1.9	0.28	7.2	0.21	23	-1.7
	BC	35	24	2.6	0.34	9.8	0.25	43	-34
C3	Experimental	11.4	13.1	1.13	0.183	6.08	0.175	-	-
	MAC	8.7	6.3	0.50	0.078	2.0	0.070	53	53
	BC	11	6.9	1.3	0.14	3.5	0.073	32	27
C4	Experimental	38.4	64.5	11.8	2.93	89.2	3.71	-	-
	MAC	23	22	2.5	0.35	8.6	0.30	76	76
	BC	41	46	4.3	0.56	10	0.20	61	58

¹ MAPE = mean absolute percentage error. ² MPE = mean percentage error.

As can be observed from Table 7, the experimental and predicted permeability coefficients for C2 and C3, in general, are close, while for C1 and C4, the predicted values are lower than the experimental ones.

It has been previously shown that the BC method is more accurate, as it discriminates the bonds between the main chain and side groups that contribute significantly to polymer rigidity [59]. We can observe the same picture in Table 7, as follows: MAPEs and MPEs are mainly lower for BC, except for the C2 polymer. This may be due to a shared tendency of MAC and BC to overestimate increments for fluorine-containing fragments and, as a result, overestimate P for fluorine-containing polymers [72–74].

Though the MAC and BC methods are completely statistical, there is a way to explain some differences in the predictions for C1–C4 polymers via increment values [72]. Let us consider C1/C2 and C3/C4 polymer pairs and the less-accurate MAC method. It can be observed that the permeability coefficient is predicted to be higher for C2 than for C1, which is consistent with the experimental data. Here, one can assume that the –CF₃ group introduction into the structure as these groups decreases the interchain interactions [68] and leads to the polymer free volume being higher. This is indeed so for the predicted values, as the –CF₃ side group has a high positive contribution to P, while the –CH₃ side group has a slight negative contribution to P. It also may be the reason why the error of the C1 prediction is higher; according to the literature [75–82], –CH₃ introduction into a polymer structure affects gas permeability in an unclear manner, even the position of the –CH₃ group introduced affects gas permeability in opposite ways [81]. So, there is a high possibility that this ambiguity leads to the –CH₃ group increment being underestimated, which, in turn, will give a lower level of predicted permeability for polymers where –CH₃ introduction is increasing the permeability.

It is also worth mentioning that the model used splits the polymer in a manner where –CH₃ is a single side-group atom (with hydrogen neighboring atoms), while –CF₃ is a side-group C atom (with non-hydrogen neighboring atoms) and three side-group F atoms. Returning to Figure 3, this is the moment that should be considered carefully for optimization of the splitting process used. The software now does not discriminate between the –F atom being a substituting atom at the fluorinated phenyl-group or –CF₃ group, and does not discriminate between side-group C atoms in the tert-butyl group or –CF₃ group. However, it is important to perform analysis showing if it is appropriate or not.

As for the C3–C4 pair, first, it is worth mentioning that data from [69,70] were used in the training dataset, so it is only expected that the predictions for this polymer will be more accurate. Both models (MAC and BC) predict C4 permeability to be higher than that of C3, which is in accordance with the measured permeability coefficients. However, the

ratio $P(C4)/P(C3)$ for the actual values is significantly higher than that for the predicted ones (Table 7). The difference between the C3 and C4 repeating units is in two additional phenyl-rings in C3, and also in the $-O-$ and $>C=O$ links in the main chain of the latter (Table 2). Phenyl rings do not lead to a high difference, because their higher number in C3 is compensated by normalization on molecular weight. So, $-O-$ and $>C=O$ fragments seem to contribute to the predicted permeability difference. As $-O-$ and $>C=O$ (combined $>C=$ and $=O$ atoms) have negative contributions to gas permeability, C3 permeability being lower than that of C4 seems logical. However, the ratio $P(C4)/P(C3)$ difference can only be explained by the overestimation of negative $-O-$ and $=O$ absolute values ($>C=$ fragment has a positive value, so it is out of the question), and underestimation of other fragments positive increments. These should be slightly modified, so that they were compensated in the same way as they are now in the C3 structure, while making C4 (where no $-O-$ and non-phthalide $=O$ are presented) permeability higher. It leads us to the need of closer increments investigation, in order to make MAC and BC prediction methods more accurate and universal. Table 8 presents the experimental gas diffusion coefficients $D \cdot 10^8$ ($\text{cm}^2 \cdot \text{s}^{-1}$) in synthesized polymers at 35 °C, and predicted data for the same polymers.

Table 8. Experimental gas diffusion coefficients $D \cdot 10^8$ ($\text{cm}^2 \cdot \text{s}^{-1}$) in synthesized polymers at 35 °C and predicted data for the same polymers.

Polymer	Type of Data	O ₂	N ₂	CO ₂	CH ₄	MAPE, %	MPE, %
C1	Experimental	2.6	0.89	0.71	0.17	-	-
	MAC	1.3	0.4	0.9	0.18	34	12
	BC	1.5	0.44	0.7	0.18	25	15
C2	Experimental	6.0	1.8	1.8	0.45	-	-
	MAC	4.7	1.7	4.1	0.59	45	-21
	BC	5.4	1.9	2.7	0.50	18	-9
C3	Experimental	1.9	0.5	0.55	0.11	-	-
	MAC	2	0.53	0.77	0.11	13	-8
	BC	1.8	1.4	1.2	0.25	107	-69
C4	Experimental	13	4.4	4.6	1.1	-	-
	MAC	4.8	1.1	1.3	0.13	75	50
	BC	2.4	12	9.0	0.97	91	-28

As can be observed from Table 8, the predicted diffusion coefficients for all the PAEKs (C1–C3) are close to the experimental ones, and for C4, there is a large spread between the two methods; BC, in general, predicts larger D , while MAC predicts the smaller ones. In this case, the BC method does not show the expected accuracy, as there are more different increments for this method than for MAC, and it leads to the equation system being less overdetermined than is needed for the method to be precise. Overall, the database [15] does not contain as many diffusion coefficient values as permeability coefficient values, so the prediction accuracy drops [38]. Figure 7 shows the comparison of experimental and predicted data in the diagrams $P_{\text{pred}} = f(P_{\text{exp}})$ (Figure 7a) and $D_{\text{pred}} = f(D_{\text{exp}})$ (Figure 7b).

As can be observed from Figure 7, generally, the scatter of the experimental and predicted data for C1–C3 fits into the half order of magnitude value, which, essentially, corresponds to an average accuracy of predictions for MAC for separate classes of polymers [29,32,35], and exceeds the accuracy of the predictions as MAC and BC for the entire dataset [38]. The predicted values for C4 are out of the range of the half order of magnitude, but remain within the range of one order of magnitude deviation, inherent of the accuracy of the predictions of both MAC and BC over the entire dataset [38]. Apparently, this behavior for C4 is caused by the abnormal rigidity of the polymer and the lack of representatives of such a class of polymers in the whole dataset, which naturally affects the accuracy of predictions by the group contribution method.

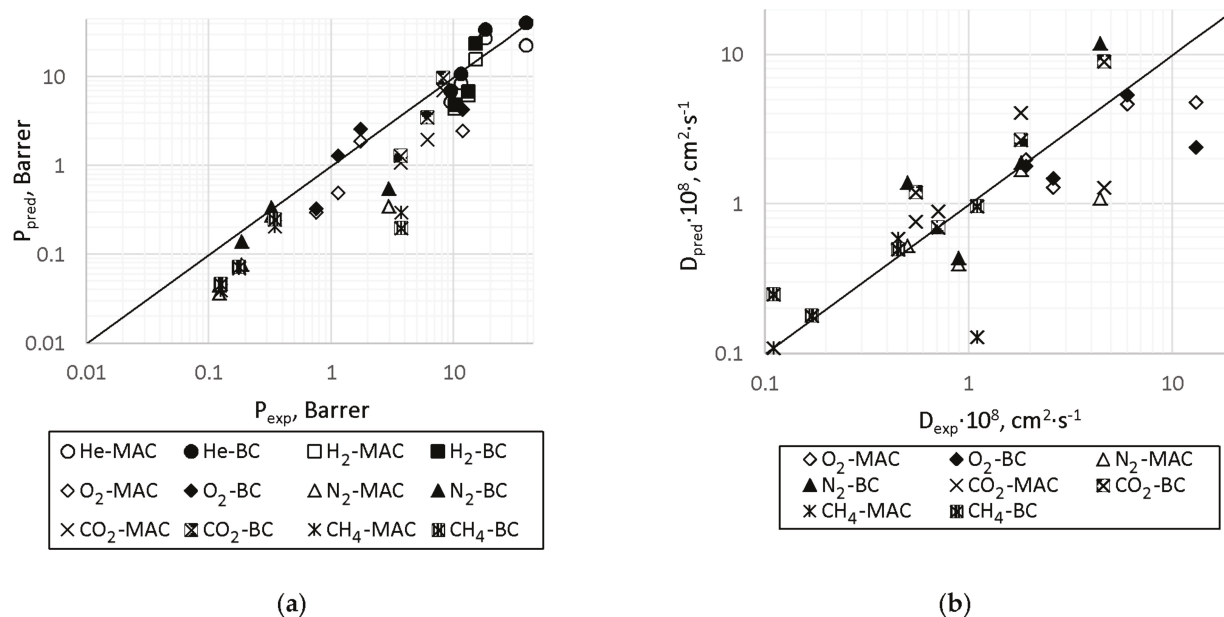


Figure 7. Comparison diagram of predicted and experimental values of permeability coefficient (a) and diffusion coefficient (b).

The solubility coefficients, predicted using the SPCSBP method, are presented in Table 9. These values were compared to the solubility coefficients calculated by the MAC and BC methods (Table 9), as P_{pred}/D_{pred} , where P_{pred} and D_{pred} are the predicted permeability and diffusion coefficients, respectively, obtained via the MAC or BC methods. The experimental solubility coefficients, obtained as P/D (both parameters extrapolated to 35 °C [64]), are also present in Table 9. It should be noticed that the extrapolation of P and D to 35 °C was performed by the method from [64], using weak correlations ($R^2 = 0.25\text{--}0.66$), which might lead to a high error in the P (35 °C) and D (35 °C) calculation. Therefore, the S (35 °C) calculation error may also be high. However, to our knowledge, the method from [64] is the only method to extrapolate experimental values of P and D to 35 °C when temperature dependences are unavailable. %clearpage

Table 9. Experimental gas solubility coefficients $S \cdot 10^3$ ($\text{cm}^3(\text{STP}) \cdot \text{cm}^{-3} \cdot \text{cmHg}^{-1}$) in synthesized polymers at 35 °C and predicted data for the same polymers.

Polymer	Type of Data	He	H_2	O_2	N_2	CO_2	CH_4	MAPE ¹ , %	MPE ² , %
C1	Experimental	0.25	1.0	2.9	1.3	52	7.3	-	
	MAC	-	-	2.3	0.93	12	2.2	50	33
	BC	-	-	2.2	1.0	19	2.6	44	30
	SPCSBP	0.76	2.4	7.8	5.9	77	18	175	-175
C2	Experimental	0.49	1.0	2.9	1.8	44	7.7	-	
	MAC	-	-	4.0	1.7	18	3.6	40	13
	BC	-	-	4.8	1.8	36	5.0	30	-3
	SPCSBP	2.1	4.5	14	11	140	39	362	-362
C3	Experimental	0.40	1.4	5.9	3.7	110	15	-	
	MAC	-	-	2.5	1.5	26	6.4	63	42
	BC	-	-	7.2	1.0	29	2.9	63	34
	SPCSBP	1.2	2.9	8.3	7.6	100	25	86	-84
C4	Experimental	0.89	2.3	9.1	6.6	190	33	-	
	MAC	-	-	5.2	3.2	66	23	47	65
	BC	-	-	18	0.47	11	2.1	94	64
	SPCSBP	1.2	4.0	12	12	140	32	42	-32

It is worth noting that the MAPEs and MPEs presented in Tables 7–9 were calculated for each of the four polymers investigated. MAPEs were also calculated for individual

regressions for different gases using all the validation set of polymers. They were the following: He—100%, H₂—56%, O₂—53%, N₂—59%, CO₂—67%, CH₄—77%. It can be observed that though the overall MAPEs are satisfactory, some disturbingly large MAPEs were obtained for some of the individual polymers (MAPE for C1 is 175% and for C2 is as great as 362%).

The comparison diagram $S_{\text{pred}} = f(S_{\text{exp}})$ is presented in Figure 8.

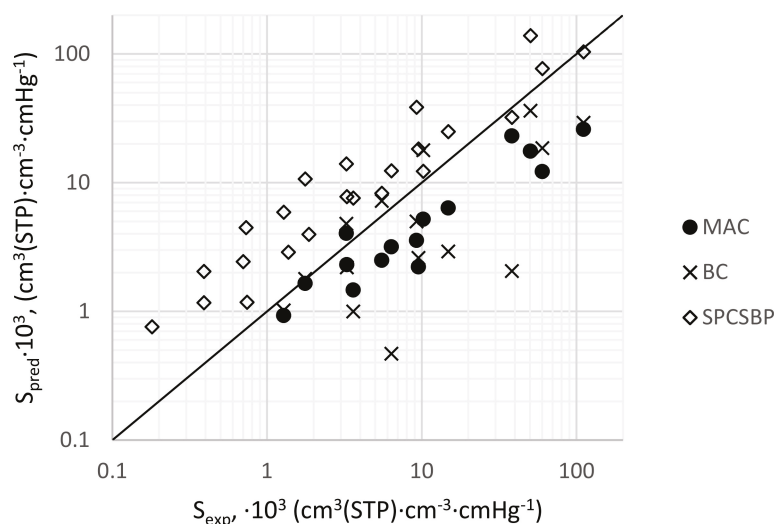


Figure 8. Comparison diagram of predicted and experimental values of solubility coefficient.

As is demonstrated in Figure 8, the MAC/BC and SPCSBP methods predictions are within one order of magnitude (except two points obtained by the BC method) compared to the experimental values. This level of prediction accuracy is not quite satisfactory for the solubility coefficient; however, some interesting observations can be made for further development of the methods. It is worth mentioning that MAC/BC and SPCSBP methods have shown opposite deviations; mostly negatively in the case of MAC/BC and mostly positively in the case of SPCSBP. Using the MPE calculation results, one can clearly see that the mostly underestimated (positive MPE numbers) values of P_{pred} combined with the overestimated (negative MPE numbers) values of D_{pred} lead to the expected noticeable S underestimation.

The SPCSBP method has more physical sense, as it includes longer-chain fragments modeling, and is based on the theory connecting polymer and gas surface areas with gas solubility in polymers [83]. However, if one compares the prediction errors for the polymers under discussion, it is obvious that SPCSBP gives good solubility coefficient predictions for C3 and C4, while there are significant errors observed for C1 and C2. The main difference between C3–C4 and C1–C2 polymers is in the presence of a phthalide group in the former pair, and the presence of a $-\text{C}(\text{CH}_3)_2$ or $-\text{C}(\text{CF}_3)_2$ group in the latter. We have calculated MAPE for poly(arylene ether ketone)s with a phthalide group and without it present in the training dataset used. They were 93% and 14% for $-\text{C}(\text{CH}_3)_2$ or $-\text{C}(\text{CF}_3)_2$ -containing and phthalide-containing poly(arylene ether ketone)s, respectively. It seems that the error of the method is also persistent for $-\text{C}(\text{CH}_3)_2$ or $-\text{C}(\text{CF}_3)_2$ -containing poly(arylene ether ketone)s, because MAPE for such polymers is six times higher than for the others. A possible explanation of the phenomenon might be associated with the circumstances that (i) the indices used in the SPCSBP method do not describe the peculiarities of the $-\text{C}(\text{CH}_3)_2$ or $-\text{C}(\text{CF}_3)_2$ groups in poly(arylene ether ketone)s structures, and their effect on gas solubility; (ii) experimental data for poly(arylene ether ketone)s with such fragments is not sufficient for regression training. All of these issues demand further investigation. This will include the addition of new fragment indices into the regression, application of the clustering method from [65] with regression building for

separate clusters, and also comparison of different oligomer conformations obtained by the SPCSBP method and molecular modeling method from [84–87].

4. Conclusions

The poly(arylene ether ketone)s and polyarylene with propylidene and phthalide moieties, with high glass transition temperatures and fractional free volumes, were synthesized. The introduction of hexafluoropropylidene (C2) and phthalide (C3) groups was shown to increase the glass transition temperature, gas permeability, and fractional free volume, when compared to the C1 polymer, due to the increase in the rigidity of the polymer chain and interchain interactions. It was demonstrated that a bulky phthalide group acts differently when introduced into a rigid or flexible main chain, and can lead to the formation of a kinked structure in the former case. However, increase of permeability and diffusion coefficients for such kinked structure is limited compared to well-known kinked polymers (PIM-like, Tröger base polymers, iptycene-based polymers, etc.), due to an increase in the interchain interactions caused by the high dipole moment of the phthalide group and compaction of the structure. Group contribution methods (MAC and BC) demonstrated (i) the same qualitative trends for the predicted gas permeabilities and diffusivities as the ones observed for the experimental data, and (ii) reasonable agreement of the predicted parameters with the experimental ones for all the polymers under investigation, except polydiphelenephthalide (C4). The latter is attributed to the overestimation of negative increments of $-O-$ and $=O$ fragments and the underestimation of positive increments of other fragments, present in the C4 polymer. The gas solubility coefficients obtained by the SPCSBP method have sufficient forecasting power for phthalide-containing polymers, while the opposite is true for propylidene-based PAEKs. This fact demands additional investigation of the influence of $-C(CH_3)_2$ and $-C(CF_3)_2$ bridges in the structure of polymers of different classes on geometrical indices in the framework of the SPCSBP approach.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/membranes11090677/s1>. Table S1. Chemical shifts and signal multiplicity in 1H NMR spectra for samples C1–C4. Table S2. Chemical shifts and signal multiplicity in ^{13}C NMR spectrum for samples C1–C4.

Author Contributions: Conceptualization, S.S. and A.A.; methodology, S.S., M.B., N.B., V.R. and O.M.; software, O.M.; validation, N.B. and V.R.; formal analysis, O.M. and A.A.; investigation, V.S., M.B., S.C., R.N., V.R. and O.M.; resources, V.S. and S.C.; writing—original draft preparation, A.A.; writing—review and editing, V.R., N.B. and O.M.; supervision, S.S. and A.A. All authors have read and agreed to the published version of the manuscript.

Funding: The work was carried out within the framework of the State Tasks of INEOS RAS and TIPS RAS. O.A. Miloserdov is grateful for the financial support of the Russian Foundation for Basic Research in the framework of research project 19-37-90004. DSC measurements were performed with the financial support from Ministry of Science and Higher Education of Russian Federation using the equipment from the Center for Molecular Composition Studies of INEOS RAS.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Yampolskii, Y.; Pinnau, I.; Freeman, B. *Materials Science of Membranes for Gas and Vapor Separation*; John Wiley & Sons, Ltd.: Chichester, UK, 2006. [CrossRef]
2. Hägg, M.-B.; He, X. Chapter 15. Carbon Molecular Sieve Membranes for Gas Separation. In *Membrane Engineering for the Treatment of Gases: Gas-Separation Problems Combined with Membrane Reactors*; Royal Society of Chemistry: London, UK, 2011; pp. 162–191. [CrossRef]

3. Ma, Y.H.; Akis, B.C.; Ayturk, M.E.; Guazzone, F.; Engwall, E.E.; Mardilovich, I.P. Characterization of Intermetallic Diffusion Barrier and Alloy Formation for Pd/Cu and Pd/Ag Porous Stainless Steel Composite Membranes. *Ind. Eng. Chem. Res.* **2004**, *43*, 2936–2945. [CrossRef]
4. Yampolskii, Y.P.; Starannikova, L.E.; Belov, N.A. Hybrid Gas Separation Polymeric Membranes Containing Nanoparticles. *Pet. Chem.* **2014**, *54*, 637–651. [CrossRef]
5. Baker, R.W.; Low, B.T. Gas Separation Membrane Materials: A Perspective. *Macromolecules* **2014**, *47*, 6999–7013. [CrossRef]
6. Matteucci, S.; Yampolskii, Y.; Freeman, B.D.; Pinnau, I. Transport of Gases and Vapors in Glassy and Rubbery Polymers. In *Materials Science of Membranes for Gas and Vapor Separation*; Yampolskii, Y., Pinnau, I., Freeman, B., Eds.; John Wiley & Sons, Ltd.: Chichester, UK, 2006; pp. 1–47. [CrossRef]
7. Robeson, L.M. Correlation of Separation Factor versus Permeability for Polymeric Membranes. *J. Membr. Sci.* **1991**, *62*, 165–185. [CrossRef]
8. Robeson, L.M. The Upper Bound Revisited. *J. Membr. Sci.* **2008**, *320*, 390–400. [CrossRef]
9. Yampolskii, Y. Polymeric Gas Separation Membranes. *Macromolecules* **2012**, *45*, 3298–3311. [CrossRef]
10. Askadskij, A.A. *Computational Materials Science of Polymers*; Cambridge International Science Publ.: Cambridge, UK, 2003.
11. Masuda, T.; Nagai, K. Synthesis and Permeation Properties of Substituted Polyacetylenes for Gas Separation and Pervaporation. In *Materials Science of Membranes for Gas and Vapor Separation*; Yampolskii, Y., Pinnau, I., Freeman, B., Eds.; John Wiley & Sons, Ltd.: Chichester, UK, 2006; pp. 231–250. [CrossRef]
12. Sanders, D.F.; Smith, Z.P.; Guo, R.; Robeson, L.M.; McGrath, J.E.; Paul, D.R.; Freeman, B.D. Energy-Efficient Polymeric Gas Separation Membranes for a Sustainable Future: A Review. *Polymer* **2013**, *54*, 4729–4761. [CrossRef]
13. Lee, W.H.; Seong, J.G.; Hu, X.; Lee, Y.M. Recent Progress in Microporous Polymers from Thermally Rearranged Polymers and Polymers of Intrinsic Microporosity for Membrane Gas Separation: Pushing Performance Limits and Revisiting Trade-off Lines. *J. Polym. Sci.* **2020**, *58*, 2450–2466. [CrossRef]
14. Wang, S.; Li, X.; Wu, H.; Tian, Z.; Xin, Q.; He, G.; Peng, D.; Chen, S.; Yin, Y.; Jiang, Z.; et al. Advances in High Permeability Polymer-Based Membrane Materials for CO₂ Separations. *Energy Environ. Sci.* **2016**, *9*, 1863–1890. [CrossRef]
15. TIPS RAS Database “Gas Separation Parameters of Glassy Polymers”; Informregister of the Russian Federation; 1998; No. 3585.
16. Membrane Society of Australasia. Database “Polymer Gas Separation Membranes”. Available online: <https://www.membrane-australasia.org/polymer-gas-separation-membranes/> (accessed on 30 July 2021).
17. Robeson, L. Polymer membranes for gas separation. *Curr. Opin. Solid State Mater. Sci.* **1999**, *4*, 549–552. [CrossRef]
18. Freeman, B.D. Basis of Permeability/Selectivity Tradeoff Relations in Polymeric Gas Separation Membranes. *Macromolecules* **1999**, *32*, 375–380. [CrossRef]
19. Alentiev, A.Y.; Yampolskii, Y.P. Free Volume Model and Tradeoff Relations of Gas Permeability and Selectivity in Glassy Polymers. *J. Membr. Sci.* **2000**, *165*, 201–216. [CrossRef]
20. Alent’ev, A.Y.; Yampolskii, Y.P.; Vidyakin, M.N.; Lazareva, Y.N. Selection of Membrane Materials for Separation of H₂-Containing Mixtures: Database Analysis. *Polym. Sci. Ser. A* **2006**, *48*, 1120–1127. [CrossRef]
21. Robeson, L.M.; Freeman, B.D.; Paul, D.R.; Rowe, B.W. An Empirical Correlation of Gas Permeability and Permselectivity in Polymers and Its Theoretical Basis. *J. Membr. Sci.* **2009**, *341*, 178–185. [CrossRef]
22. Malykh, O.V.; Golub, A.Y.; Teplyakov, V.V. Polymeric Membrane Materials: New Aspects of Empirical Approaches to Prediction of Gas Permeability Parameters in Relation to Permanent Gases, Linear Lower Hydrocarbons and Some Toxic Gases. *Adv. Colloid Interface Sci.* **2011**, *164*, 89–99. [CrossRef]
23. Ryzhikh, V.E.; Alent’ev, A. Yu.; Yampol’skii, Yu. P. Relation of Gas-Transport Parameters of Amorphous Glassy Polymers to Their Free Volume: Positron Annihilation Study. *Polym. Sci. Ser. A* **2013**, *55*, 244–252. [CrossRef]
24. Alentiev, A.; Yampolskii, Y. Correlation of Gas Permeability and Diffusivity with Selectivity: Orientations of the Clouds of the Data Points and the Effects of Temperature. *Ind. Eng. Chem. Res.* **2013**, *52*, 8864–8874. [CrossRef]
25. Robeson, L.M.; Smith, Z.P.; Freeman, B.D.; Paul, D.R. Contributions of Diffusion and Solubility Selectivity to the Upper Bound Analysis for Glassy Gas Separation Membranes. *J. Membr. Sci.* **2014**, *453*, 71–83. [CrossRef]
26. Swaidan, R.; Ghanem, B.; Pinnau, I. Fine-Tuned Intrinsically Ultramicroporous Polymers Redefine the Permeability/Selectivity Upper Bounds of Membrane-Based Air and Hydrogen Separations. *ACS Macro Lett.* **2015**, *4*, 947–951. [CrossRef]
27. Comesaña-Gándara, B.; Chen, J.; Bezzu, C.G.; Carta, M.; Rose, I.; Ferrari, M.-C.; Esposito, E.; Fuoco, A.; Jansen, J.C.; McKeown, N.B. Redefining the Robeson Upper Bounds for CO₂/CH₄ and CO₂/N₂ Separations Using a Series of Ultrapervious Benzotriptycene-Based Polymers of Intrinsic Microporosity. *Energy Environ. Sci.* **2019**, *12*, 2733–2740. [CrossRef]
28. Alent’ev, A.Y.; Ryzhikh, V.E.; Belov, N.A. Highly Permeable Polyheteroarylenes for Membrane Gas Separation: Recent Trends in Chemical Structure Design. *Polym. Sci. Ser. C* **2020**, *62*, 238–258. [CrossRef]
29. Alentiev, A.; Yampolskii, Y. Prediction of Gas Permeation Parameters of Polymers. In *Materials Science of Membranes for Gas and Vapor Separation*; Yampolskii, Y., Pinnau, I., Freeman, B., Eds.; John Wiley & Sons, Ltd.: Chichester, UK, 2006. [CrossRef]
30. Robeson, L.A.; Smith, C.D.; Langsam, M. Group Contribution Approach to Predict Permeability and Permselectivity of Aromatic Polymers. *J. Membr. Sci.* **1997**, *132*, 33–54. [CrossRef]
31. Park, J.Y.; Paul, D.R. Correlation and Prediction of Gas Permeability in Glassy Polymer Membrane Materials via a Modified Free Volume Based Group Contribution Method. *J. Membr. Sci.* **1997**, *125*, 23–39. [CrossRef]

32. Yampolskii, Y.; Shishatskii, S.; Alentiev, A.; Loza, K. Group Contribution Method for Transport Property Predictions of Glassy Polymers: Focus on Polyimides and Polynorbornenes. *J. Membr. Sci.* **1998**, *149*, 203–220. [CrossRef]
33. Laciak, D.V.; Robeson, L.M.; Smith, C.D. Group Contribution Modeling of Gas Transport in Polymeric Membranes. In *Polymer Membranes for Gas and Vapor Separation: Chemistry and Materials Science*; ACS Symposium Series; Freeman, B.D., Pinnau, I., Eds.; American Chemical Society: Washington, DC, USA, 1999; Volume 733. [CrossRef]
34. Alentiev, A.Y.; Loza, K.A.; Yampolskii, Y.P. Development of the Methods for Prediction of Gas Permeation Parameters of Glassy Polymers: Polyimides as Alternating Co-Polymers. *J. Membr. Sci.* **2000**, *167*, 91–106. [CrossRef]
35. Kubica, P.; Wolinska-Grabczyk, A. Correlation between Cohesive Energy Density, Fractional Free Volume, and Gas Transport Properties of Poly(ethylene-co-vinyl acetate) Materials. *Int. J. Polym. Sci.* **2015**, *2015*, 1–8. [CrossRef]
36. Alentiev, A.; Yampolskii, Y.; Ryzhikh, V.; Tsarev, D. The Database “Gas Separation Properties of Glassy Polymers” (Topchiev Institute): Capabilities and Prospects. *Petrol. Chem.* **2013**, *53*, 554–558. [CrossRef]
37. Velioglu, S.; Tantekin-Ersolmaz, S.B.; Chew, J.W. Towards the Generalization of Membrane Structure-Property Relationship of Polyimides and Copolyimides: A Group Contribution Study. *J. Membr. Sci.* **2017**, *543*, 233–254. [CrossRef]
38. Ryzhikh, V.; Tsarev, D.; Alentiev, A.; Yampolskii, Y. A Novel Method for Predictions of the Gas Permeation Parameters of Polymers on the Basis of Their Chemical Structure. *J. Membr. Sci.* **2015**, *487*, 189–198. [CrossRef]
39. Velioglu, S.; Tantekin-Ersolmaz, S.B. Prediction of Gas Permeability Coefficients of Copolyimides by Group Contribution Methods. *J. Membr. Sci.* **2015**, *480*, 47–63. [CrossRef]
40. Surgi, M.R.; Polak, A.J.; Sundahl, R.C. Description of Oxygen Permeability in Various High Polymers Using a Graph Theoretical Approach. *J. Polym. Sci. A Polym. Chem.* **1989**, *27*, 2761–2776. [CrossRef]
41. Bicerano, J. *Prediction of Polymer Properties*, 3rd ed.; Plastics Engineering, Marcel Dekker: New York, NY, USA, 2002.
42. Zhong, C.; Yang, C. Approach for the Calculation of High-Order Connectivity Indices of Polymers and Its Application. *J. Polym. Sci. B Polym. Phys.* **2002**, *40*, 401–407. [CrossRef]
43. Goubko, M.; Miloserdov, O.; Yampolskii, Y.; Alentiev, A.; Ryzhikh, V. A Novel Model to Predict Infinite Dilution Solubility Coefficients in Glassy Polymers. *J. Polym. Sci. B Polym. Phys.* **2017**, *55*, 228–244. [CrossRef]
44. Goubko, M.V.; Miloserdov, O.A.; Yampolskii, Y.P.; Ryzhikh, V.Y. Prediction of Solubility Parameters of Light Gases in Glassy Polymers on the Basis of Simulation of a Short Segment of a Polymer Chain. *Polym. Sci. Ser. A* **2019**, *61*, 718–732. [CrossRef]
45. Wessling, M. Relaxation Phenomena in Dense Gas Separation Membranes. Ph.D. Thesis, University of Twente, Twente, The Netherlands, 1993.
46. Barnett, J.W.; Bilchak, C.R.; Wang, Y.; Benicewicz, B.C.; Murdock, L.A.; Bereau, T.; Kumar, S.K. Designing Exceptional Gas-Separation Polymer Membranes Using Machine Learning. *Sci. Adv.* **2020**, *6*, eaaz4301. [CrossRef] [PubMed]
47. Alentiev, A.; Economou, I.G.; Finkelshtein, E.; Petrou, J.; Raptis, V.E.; Sanopoulou, M.; Soloviev, S.; Ushakov, N.; Yampolskii, Y. Transport Properties of Silmethylene Homo-Polymers and Random Copolymers: Experimental Measurements and Molecular Simulation. *Polymer* **2004**, *45*, 6933–6944. [CrossRef]
48. Heuchel, M.; Hofmann, D.; Pullumbi, P. Molecular Modeling of Small-Molecule Permeation in Polyimides and Its Correlation to Free-Volume Distributions. *Macromolecules* **2004**, *37*, 201–214. [CrossRef]
49. Hofmann, D.; Heuchel, M.; Yampolskii, Y.; Khotimskii, V.; Shantarovich, V. Free Volume Distributions in Ultrahigh and Lower Free Volume Polymers: Comparison between Molecular Modeling and Positron Lifetime Studies. *Macromolecules* **2002**, *35*, 2129–2140. [CrossRef]
50. Theodorou, D.N. Principles of Molecular Simulation of Gas Transport in Polymers. In *Materials Science of Membranes for Gas and Vapor Separation*; Yampolskii, Y., Pinnau, I., Freeman, B., Eds.; John Wiley & Sons, Ltd.: Chichester, UK, 2006; pp. 49–94. [CrossRef]
51. Neyertz, S.; Douanne, A.; Brown, D. Effect of Interfacial Structure on Permeation Properties of Glassy Polymers. *Macromolecules* **2005**, *38*, 10286–10298. [CrossRef]
52. Neyertz, S. Gas Transport in Dense Polymeric Membranes, Molecular Dynamics Simulations. In *Encyclopedia of Membrane Science and Technology*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2013; p. emst101. [CrossRef]
53. Tocci, E.; De Lorenzo, L.; Bernardo, P.; Clarizia, G.; Bazzarelli, F.; Mckeown, N.B.; Carta, M.; Malpass-Evans, R.; Friess, K.; Pilnáček, K.; et al. Molecular Modeling and Gas Permeation Properties of a Polymer of Intrinsic Microporosity Composed of Ethanoanthracene and Tröger’s Base Units. *Macromolecules* **2014**, *47*, 7900–7916. [CrossRef]
54. Bisoi, S.; Mandal, A.K.; Padmanabhan, V.; Banerjee, S. Aromatic Polyamides Containing Trityl Substituted Triphenylamine: Gas Transport Properties and Molecular Dynamics Simulations. *J. Membr. Sci.* **2017**, *522*, 77–90. [CrossRef]
55. Gartner, T.E.; Jayaraman, A. Modeling and Simulations of Polymers: A Roadmap. *Macromolecules* **2019**, *52*, 755–786. [CrossRef]
56. Gooneie, A.; Schuschnigg, S.; Holzer, C. A Review of Multiscale Computational Methods in Polymeric Materials. *Polymers* **2017**, *9*, 16. [CrossRef]
57. Salazkin, S.N.; Shaposhnikova, V.V. Poly(Arylene Ether Ketones): Thermostable, Heat Resistant, and Chemostable Thermoplastics and Prospects for Designing Various Materials on Their Basis. *Polym. Sci. Ser. C* **2020**, *62*, 111–123. [CrossRef]
58. Shaposhnikova, V.V.; Salazkin, S.N. Synthesis and Properties of Poly(Arylene Ether Ketones). *Russ. Chem. Bull.* **2014**, *63*, 2213–2223. [CrossRef]
59. Shaposhnikova, V.V.; Salazkin, S.N.; Sergeev, V.A.; Blagodatskikh, I.V.; Dubrovina, L.V.; Sakunts, A.A.; Pavlova, S.-S.A. General Features of the Reaction of 4,4′-Difluorobenzophenone with Potassium Diphenoxide of 2,2-Bis (4-Hydroxyphenyl)Propane. *Russ. Chem. Bull.* **1996**, *45*, 2397–2401. [CrossRef]

60. Zolotukhin, M.G.; Kovardakov, V.A.; Salazkin, S.N.; Rafikov, S.R. Some Features of the Synthesis of Polydiphenylene Phthalide by Condensation of P-(3-Chloro-3-Phthalidyl) Diphenyl. *Polym. Sci. USSR* **1984**, *26*, 1355–1361. [CrossRef]
61. Shaposhnikova, V.V.; Salazkin, S.N.; Donetskii, K.I.; Gorshkov, G.V.; Sharapov, D.S.; Mamedova, I.A.; Petrovskii, P.V.; Askadskii, A.A.; Bychko, K.A.; Kazantseva, V.V.; et al. Synthesis and Properties of Cardo Copoly(Arylene Ether Ketones). *Polym. Sci. Ser. A* **2002**, *44*, 563–569.
62. Fatykhov, A.A.; Sedova, E.A.; Egorov, A.E.; Salazkin, S.N.; Kraikin, V.A. NMR Study of Phthalide-Type Poly(Phenylene)s. Symmetry and Additivity: NMR Study of Phthalide-Type Poly(Phenylene)s. Symmetry and Additivity. *Magn. Reson. Chem.* **2017**, *55*, 958–966. [CrossRef]
63. Bondi, A.A. *Physical Properties of Molecular Crystals, Liquids, and Glasses*; Wiley Series on the Science and Technology of Materials; Wiley: New York, NY, USA, 1968.
64. Yampolskii, Y.; Shishatskii, S.; Alentiev, A.; Loza, K. Correlations with and Prediction of Activation Energies of Gas Permeation and Diffusion in Glassy Polymers. *J. Membr. Sci.* **1998**, *148*, 59–69. [CrossRef]
65. Miloserdov, O. Classifying Amorphous Polymers for Membrane Technology Basing on Accessible Surface Area of Their Conformations. *Adv. Syst. Sci. Appl.* **2020**, *3*, 91–104. [CrossRef]
66. Lee, B.; Richards, F.M. The Interpretation of Protein Structures: Estimation of Static Accessibility. *J. Mol. Biol.* **1971**, *55*, 379–400. [CrossRef]
67. Salazkin, S.N.; Rafikov, S.R.; Zolotukhin, M.G.; Tolstikov, G.A. New Way of Synthesis of Aromatic Polymers. *Dokl. Akad. Nauk* **1982**, *262*, 355–359.
68. Hirayama, Y.; Yoshinaga, T.; Kusuki, Y.; Ninomiya, K.; Sakakibara, T.; Tamari, T. Relation of Gas Permeability with Structure of Aromatic Polyimides I. *J. Membr. Sci.* **1996**, *111*, 169–182. [CrossRef]
69. Zheng, Y.; Yang, X.; Yuan, M.; Luo, J. Synthesis and gas transport properties of novel poly(ether ether ketone)s containing fluorene group. *High Perform. Polym.* **2019**, *31*, 1173–1182. [CrossRef]
70. Wang, Z.; Chen, T.; Xu, J. Gas Transport Properties of Novel Cardo Poly(Aryl Ether Ketone)s with Pendant Alkyl Groups. *Macromolecules* **2000**, *33*, 5672–5679. [CrossRef]
71. Bondar, V.I.; Freeman, B.D.; Pinnau, I. Gas Sorption and Characterization of Poly(Ether-b-Amide) Segmented Block Copoly-mers. *J. Polym. Sci. B: Polym. Phys.* **1999**, *37*, 2463–2475.
72. Ryzhikh, V. Development of Transport Parameters of Polymer Materials Prediction Using Database. Ph.D. Thesis, Topchiev Institute of Petrochemical Synthesis of Russian Academy of Sciences, Moscow, Russia, 2014.
73. Chatterjee, R.; Kumar, A.G.; Nikiforov, R.; Ryzhikh, V.; Belov, N.; Padmanabhan, V.; Yampolskii, Y.; Banerjee, S. Novel Semi-Fluorinated Poly(Ether Imide)s with Benzyl Ether Side Groups: Synthesis, Physicochemical Characterization, Gas Transport Properties and Simulation. *Eur. Polym. J.* **2020**, *135*, 109879. [CrossRef]
74. Belov, N.; Chatterjee, R.; Nikiforov, R.; Ryzhikh, V.; Bisoi, S.; Kumar, A.G.; Banerjee, S.; Yampolskii, Y. New Poly(Ether Imide)s with Pendant Di-Tert-Butyl Groups: Synthesis, Characterization and Gas Transport Properties. *Sep. Purif. Technol.* **2019**, *217*, 183–194. [CrossRef]
75. Eastmond Geoffrey, C.; Daly John, H.; McKinnon Alexander, S.; Pethrick Richard, A. Poly(Ether Imide)s: Correlation of Positron Annihilation Lifetime Studies with Polymer Structure and Gas Permeability. *Polymer* **1999**, *40*, 3605–3610. [CrossRef]
76. Al-Masri, M.; Fritsch, D.; Kricheldorf, H.R. New Polyimides for Gas Separation. 2. Polyimides Derived from Substituted Catechol Bis(Etherphthalic Anhydride)s. *Macromolecules* **2000**, *33*, 7127–7135. [CrossRef]
77. Finkelshtein, E.S.; Makovetskii, K.L.; Gringolts, M.L.; Rogan, Y.V.; Golenko, T.G.; Starannikova, L.E.; Yampolskii, Y.P.; Shantarovich, V.P.; Suzuki, T. Addition-Type Polynorbornenes with Si(CH₃)₃ Side Groups: Synthesis, Gas Permeability, and Free Volume. *Macromolecules* **2006**, *39*, 7022–7029. [CrossRef]
78. Dorkenoo, K.D.; Pfromm, P.H.; Rezac, M.E. Gas Transport Properties of a Series of High Tg Polynorbornenes with Aliphatic Pendant Groups. *J. Polym. Sci. B Polym. Phys.* **1998**, *36*, 797–803. [CrossRef]
79. Shida, Y.; Sakaguchi, T.; Shiotsuki, M.; Sanda, F.; Freeman, B.D.; Masuda, T. Synthesis and Properties of Membranes of Poly(Diphenylacetylenes) Having Fluorines and Hydroxyl Groups. *Macromolecules* **2006**, *39*, 569–574. [CrossRef]
80. Hu, Y.; Sakaguchi, T.; Shiotsuki, M.; Sanda, F.; Masuda, T. Synthesis and Characterization of Poly(Diphenylacetylenes) Containing Both Hydroxy and Halogen/Alkyl Groups as Gas Separation Membranes. *J. Membr. Sci.* **2006**, *285*, 412–419. [CrossRef]
81. Puleo, A.C.; Muruganandam, N.; Paul, D.R. Gas Sorption and Transport in Substituted Polystyrenes. *J. Polym. Sci. B Polym. Phys.* **1989**, *27*, 2385–2406. [CrossRef]
82. Salame, M. Transport Properties of Nitrile Polymers: Properties of Nitrile Polymers. *J. Polym. Sci. C Polym. Symp.* **1973**, *41*, 1–15. [CrossRef]
83. Yampolskii, Y.; Wiley, D.; Maher, C. Novel Correlation for Solubility of Gases in Polymers: Effect of Molecular Surface Area of Gases. *J. Appl. Polym. Sci.* **2000**, *76*, 552–560. [CrossRef]
84. Mazo, M.; Balabaev, N.; Alentiev, A.; Yampolskii, Y. Molecular Dynamics Simulation of Nanostructure of High Free Volume Polymers with SiMe₃ Side Groups. *Macromolecules* **2018**, *51*, 1398–1408. [CrossRef]
85. Mazo, M.; Balabaev, N.; Alentiev, A.; Strelnikov, I.; Yampolskii, Y. Structure and Properties of High and Low Free Volume Polymers Studied by Molecular Dynamics Simulation. *Computation* **2019**, *7*, 27. [CrossRef]
86. Wang, S.; Yu, Y.; Gao, G. Non-equilibrium Molecular Dynamics Simulation on Pure Gas Permeability Through Carbon Membranes. *Chin. J. Chem. Eng.* **2006**, *14*, 164–170. [CrossRef]

87. Wang, S.-M.; Yu, Y.-X.; Gao, G.-H. Grand canonical Monte Carlo and non-equilibrium molecular dynamics simulation study on the selective adsorption and fluxes of oxygen/nitrogen gas mixtures through carbon membranes. *J. Membr. Sci.* **2006**, *271*, 140–150. [CrossRef]

Article

Assessment of Sieverts Law Assumptions and ' n ' Values in Palladium Membranes: Experimental and Theoretical Analyses

Abdulrahman Alraeesi ^{1,*} and Tracy Gardner ²

¹ Chemical and Petroleum Engineering Department, United Arab Emirates University, Al Ain P.O. Box 15551, United Arab Emirates

² Chemical and Biological Engineering Department, Colorado School of Mines, Golden, CO 80401, USA; tgardner@mines.edu

* Correspondence: a.alraeesi@uaeu.ac.ae

Abstract: Palladium and palladium alloy membranes are superior materials for hydrogen purification, removal, or reaction processes. Sieverts' Law suggests that the flux of hydrogen through such membranes is proportional to the difference between the feed and permeate side partial pressures, each raised to the 0.5 power ($n = 0.5$). Sieverts' Law is widely applied in analyzing the steady state hydrogen permeation through Pd-based membranes, even in some cases where the assumptions made in deriving Sieverts' Law do not apply. Often permeation data are fit to the model allowing the pressure exponent (n) to vary. This study experimentally assessed the validity of Sieverts' Law as hydrogen was separated from other gases and theoretically modelled the effects of pressure and temperature on the assumptions and hence the accuracy of the 0.5-power law even with pure hydrogen feed. Hydrogen fluxes through Pd and Pd-Ag alloy foils from feed mixtures (5–83% helium in hydrogen; 473–573 K; with and without a sweep gas) were measured to study the effect of concentration polarization (CP) on hydrogen permeance and the applicability of Sieverts' Law under such conditions. Concentration polarization was found to dominate hydrogen transport under some experimental conditions, particularly when feed concentrations of hydrogen were low. All mixture feed experiments showed deviation from Sieverts' Law. For example, the hydrogen flux through Pd foil was found to be proportional to the partial pressure difference ($n \approx 1$) rather than being proportional to the difference in the square root of the partial pressures ($n = 0.5$), as suggested by Sieverts' Law, indicating the high degree of concentration polarization. A theoretical model accounting for Langmuir adsorption with temperature dependent adsorption equilibrium coefficient was made and used to assess the effect of varying feed pressure from 1–136 atm at fixed temperature, and of varying temperature from 298 to 1273 K at fixed pressure. Adsorption effects, which dominate at high pressure and at low temperature, result in pressure exponents (n) values less than 0.5. With better understanding of the transport steps, a qualitative analysis of literature (n) values of 0.5, $0.5 < n < 1$, and $n > 1$, was conducted suggesting the role of each condition or step on the hydrogen transport based on the empirically fit exponent value.

Keywords: concentration polarization; palladium foil; palladium-silver membrane; permeation; hydrogen permeation; mixed feed gas; Sieverts' law; n value; transport modeling

1. Introduction

Pure hydrogen gas is considered to be a valued chemical product, due to its use in refinery processes and as a feedstock for ammonia synthesis [1,2]. Furthermore, in recent years, hydrogen has been valued as a promising form of energy storage for sporadic renewable power and as a clean fuel [3]. The conventional method for hydrogen production is primarily steam reforming of fossil fuels [4,5]. Historically, hydrogen is produced from fossil fuels, out of which 60% is from dedicated primary hydrogen-producing facilities. In the Middle East, hydrogen from natural gas (NG) costs (USD 1/kg H₂). As

far production is concerned, 71.27% of hydrogen is produced from NG, 27.27% from coal, and the remaining 1.4% is equally divided between petroleum and water electrolysis. Most recently, bio-hydrogen production has gained attention compared with fossil-based hydrogen. Biomass gasification of bio-wastes is commercially available with 88% energy conversion efficiency, while processes such as dark and photo fermentation, bio photolysis, and microbial electrolysis cell (MEC) are still under development, and the combined energy conversion efficiency of all processes does not exceed 25% [6]. The latter processes have some limitations: (i) the bio-photolysis requires an external light source and a customized bioreactor and still the hydrogen yield is low; (ii) the dark fermentation is thermodynamically limited and favors the pretreatment of certain wastes with the need of an additional separation unit for H₂ purification plus the effluent has a high BOD; (iii) the photo-fermentation is only suitable for VFA-rich waste, constrained by day-night cycle (i.e., an external source of light) and produces low hydrogen rate with low light conversion efficiency; and (iv) MEC: despite the high H₂ yield the production rate is low and there is a demand for external voltage as well as the catalyst [6,7]. The limitations can be accommodated and overcome by the use of: an efficient and properly designed bioreactor, appropriate process modifications, a suitable feedstocks, and an efficient microbial strains [8]. Moreover, because of the high H₂ diffusivity, the low density (as gas or liquid), the higher gravimetric energy content and the wider flammability limits compared to most fossil fuels; hydrogen cost and safety obstacles are there at every step of distribution, shipment, or storage. Hydrogen can be delivered as a pressurized gas, or in the liquid form, combined in an absorbing metallic alloy matrix or transported in a chemical precursor form such as lithium. Hydrogen storage-classified risk is a concern, and hence an electrochemical hydrogen storage was developed by the integration of a solid multi-walled carbon nanotube (MWCNT) electrode in a modified unitized regenerative fuel cell (URFC). The developed porous MWCNT electrode had electrochemical hydrogen storage capacity of 2.47 wt%, comparable with commercially available AB5-based hydrogen storage [9–11].

Some industrial applications such as combustion are capable to use the reformat gas mixture with no treatment, while other applications need the feed gas to be highly purified in hydrogen [12] by use of a well-known technology as the pressure swing absorption (PSA) [13]. However, this method is still suffering from complexity and relevant high energy requirements. An attractive and suitable purification alternative technology for PSA, is the use of dense palladium (Pd) metal membranes. Palladium membranes are basically considered to be a passive system, where in such system, the driving force for full separation is basically the hydrogen partial pressure across the membrane [14]. Palladium-based membranes (Pd or Pd-alloy) are unique in their relative thermal stability and hence operates at high temperatures to save the capital and the operating cost through retaining both hydrogen and carbon dioxide at high pressures [15,16]. A hydrogen separation membrane unit can be ideally applicable in gas cleaning (upstream technology) and in fuel cells and/or hydrogen turbines (downstream technology) [16]. Additionally, membranes can be combined to catalysts in order to conduct simultaneously equilibrium-limited reactions and hydrogen separation in a single unit called catalytic membrane reactor (CMR) [17]. Consequently, Palladium membranes have been often used for water gas shift and steam reforming reactions to shift the reaction and achieve high conversion and hence promote the production of highly purified hydrogen [18]. However, some limitations in palladium membranes performance have been encountered due to incorporation of less expensive materials and moving to the composite structure, permeability evaluation of impure feed gas containing hydrogen molecule, and finally optimization of the operating conditions. Therefore, transport resistances and the assumptions used in deriving the Sieverts' Law, the hydrogen flux-pressure dependence equation, to be carefully evaluated.

Hydrogen transport in palladium-based membranes starts by the adsorption of hydrogen molecules on the membrane surface, followed by dissociation into atomic hydrogen, then transition of atomic hydrogen from the surface into the bulk metal,

then atomic diffusion through the bulk metal, re-combinative desorption, and finally gas transport away from the surface to the bulk gas [19]. The existence of other gas components with hydrogen in the feed (as gas mixture) can decrease the permeation of hydrogen through the membrane [20,21]. The mixed feed, with fast hydrogen depletion in the membrane, develops a fluid phase resistance that either decreases the effective hydrogen partial pressure difference for permeation or limits the dissociative adsorption of hydrogen on the palladium surface [20]. There are several scenarios to describe the decrease of hydrogen-permeation (i) hydrogen dilution in the feed by the presence of other gas components, (ii) hydrogen depletion of the bulk feed due to hydrogen removal along the length of the membrane module, (iii) the build-up of a hydrogen-depleted layer adjacent to the membrane surface as a result of gas phase mass transport limitation, and possible competitive adsorption of mixture components on the membrane surface [22]. The Sieverts' law can be applied to predict and evaluate the hydrogen permeation flux when Pd-H₂ system considered as infinitely diluted or has "Ideal behavior", in this scenario, the hydrogen diffusion in the lattice controls permeation and, at the same time, the H-concentration in the same lattice is so low [23]. It is worth mention that the previous described conditions are essential but not sufficient for pressure exponent to be 0.5. Overall, all metal membranes are far from ideal behavior. Therefore, major deviations from the Sieverts' law have been noticed in the literature [24,25]. A main experimental finding for very thick palladium membranes, i.e., either thick Pd or ultrathin Pd composite membrane, is that the permeation behavior can considerably diverge from the Sieverts' law [24,26], and it can be related to the solubility and diffusivity in the metal lattice [27–29]. Additionally, some theoretical case studies reported a different Sieverts' pressure exponent n from the ideal value even in the presence of pure hydrogen feed [27,30,31]. Flanagan and Wang [32–34] presented a common approach to evaluate the Einstein hydrogen diffusivity (referred to as "intrinsic" or "ideal" diffusivity) and the nonideal correction from the experimental isotherms of the thermodynamic factor versus the atom ratio, in addition to the case where the excess of chemical potential is estimated by a linear function of the atom ratio. Another approach is proposed by Hara and coworkers, who established a methodology to assess the intrinsic concentration-independent hydrogen permeability and solubility by means of polynomial functions of the square root of the hydrogen partial pressure [27,35]. However, the continuous development and improvement of high-performing thin metal membranes is making the external mass transfer more and more significant and hence increase the complexity of the approach. Peters et al. (2008) [36] quantified the external mass transfer effect on hydrogen permeation through a 2.2 mm-thick Pd-alloy tubule membrane reactor system. A maximum H₂ flux of 1223 mL cm^{−2} min^{−1} was obtained at 400 °C and 26 bar pure hydrogen feed pressure while in a mixture of 50% H₂ + 50% N₂ a maximum H₂ flux of 230 mL cm^{−2} min^{−1} was at 26 bar. Even in water gas shift gas mixtures conditions a stronger influence of the dilution and the mass transfer, on the hydrogen flux, was largely observed. In general, the concentration polarization is a visible element in delaying hydrogen permeation [37,38]. Concentration polarization is generated by the stimulated concentration boundary layer along the membrane surface and this results in a lower hydrogen partial pressure at the retentate side of the membrane. The process of concentration polarization is schematically illustrated in Figure 1 across a dense palladium foil in the presence of hydrogen-helium feed mixture, where $P_{H_2,s}$ and $P_{H_2,f}$ are the partial pressure of hydrogen at the surface and in the bulk fluid, respectively.

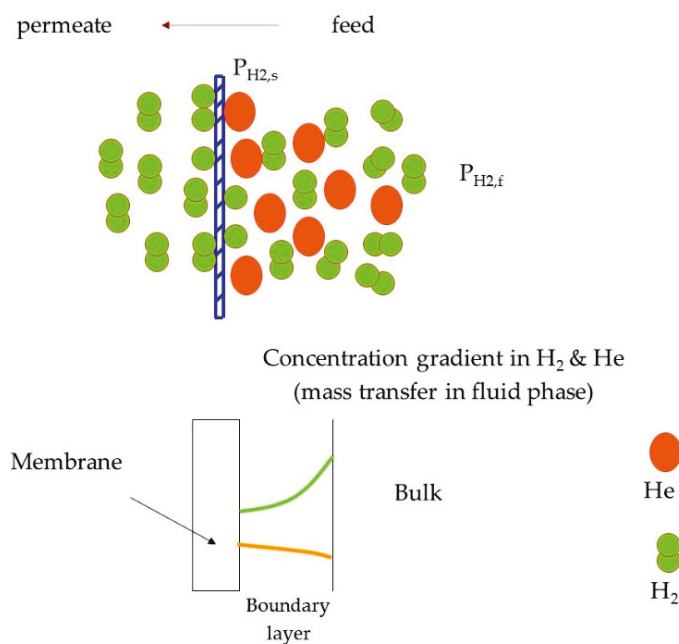


Figure 1. Schematic of hydrogen transport through a fluid phase on the feed side and then through the metal membrane.

According to this phenomena, hydrogen permeation deviates from Sieverts' law and the model of continuous stirred tank reactor (CSTR) cannot be applied, particularly close to the membrane surface zone [39], hence, the mass transfer across the Pd membrane approaches the behavior of plug flow reactor (PFR). Concentration polarization may be intensified with low feed gas flow rate, high membrane permeability and selectivity, high H_2 partial pressure difference across the membrane and at high membrane temperature [17,40]. In other words, increasing feed gas flow rate can significantly minimize the concentration polarization effect, as it flushes the fluid phase layer close to Pd surface. According to literature, the concentration polarization is a noticeable factor in retarding hydrogen permeation, where normally a pressure exponent (n) value in the range of 0.5–1.0 is reported [41–43]. If an appropriate pressure exponent is employed, the ratio of H_2 flux and H_2 partial pressure difference is characterized by a constant and one is able to identify the permeate of the tested membrane from the ratio. The pressure exponent (n), which is typically treated in the literature as an empirical fit parameter and normally an appropriate value is employed for analyzing permeation fluxes, differs from one study to another. In the current study some (n) values from literature, for a more complicated system with supported and unsupported Pd membranes in cases of pure and mixture feeds, are discussed.

Recall that the fast development of Pd-based membrane modules and the relevant applications of hydrogen purification/removal/catalytic reactions requires a better understanding of the hydrogen transport and the limitations in the Pd-based membrane structures as well as the high temperature and pressure operations. Therefore, the effect of operating conditions (T , P) on pressure exponent (n) was modeled, as well as the experimental easement of CP effect. It is worth to add here that despite the concentration polarization drawback of a lower flux, it can potentially be used as an advantage in the catalytic membrane reactor (CMR) system [44]. For example, in hydrogenation reaction, without altering the reaction pressure or temperature it is possible to adjust the feed composition and therefore lower the hydrogen penetration to the reaction zone. Controlling the hydrogen flux through the membrane would consequently controls the hydrogen coverage on the catalyst surface at permeate side, and subsequently, the selective hydrogenation reaction rate as well as reaction yield can be theoretically controlled [45–47]. Furthermore, the oxidation state of a catalyst deposited on the downstream side of a

palladium-based membrane reactor could potentially be dynamically adjusted during reaction by adjusting the hydrogen feed composition or conditions [48–50]. For example, if the catalyst is reducing too quickly, the hydrogen flow rate could be reduced by diluting the hydrogen feed more. To model and analyze hydrogen permeation in such systems, the transport mechanism must be well understood.

The current work is a fundamental study on hydrogen permeation through palladium-based membranes to experimentally and theoretically assess the assumptions in deriving the Sieverts' Law in cases of concentration polarization and diverse operating conditions. The findings of the study are used to evaluate and interpret the literature-based reported pressure exponent (n) values where it is considered an empirical fit parameter.

2. Theory

Hydrogen permeates through all dense metallic membranes including palladium-based membranes via the same mechanism as a complex multistep process [51,52]. The transport through these membranes is modeled using the solution-diffusion approach. In the solution-diffusion model, the flux of hydrogen gas through Pd-based membranes is the product of its solubility, a measure of the amount of hydrogen absorbed in the membrane under equilibrium conditions, and its diffusivity, a measure of how fast hydrogen atoms transport through the membrane [53–55].

Hydrogen permeation through palladium membranes is a complex, multi-step process, as shown in Figure 2.

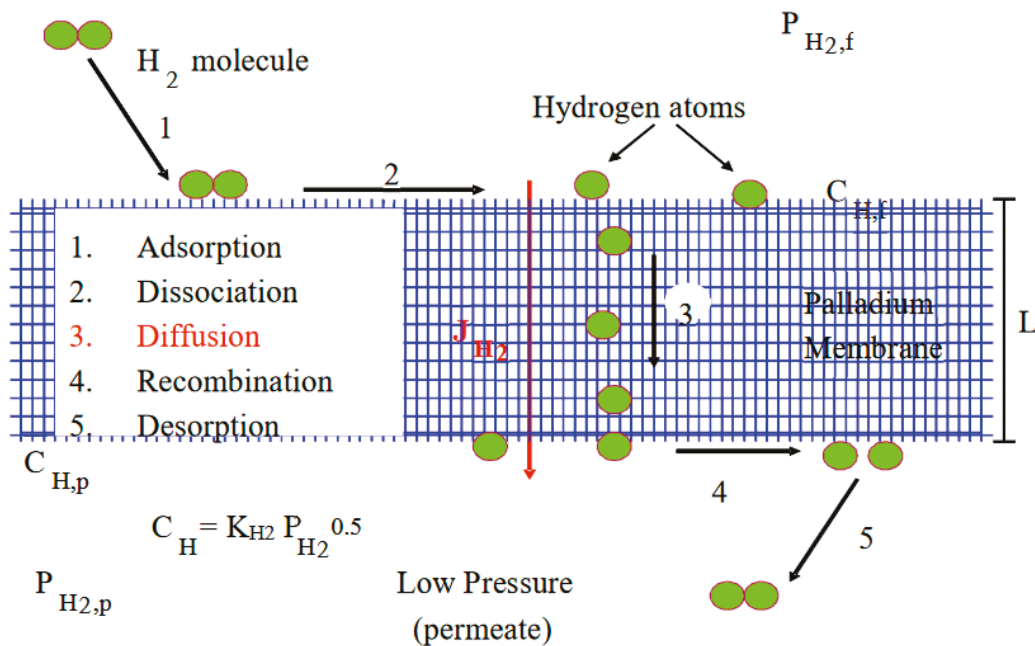


Figure 2. Schematic of hydrogen transport mechanism through Pd-based membranes.

Hydrogen molecules dissociatively adsorb on the surface (steps 1 and 2), diffuse through the bulk metal (step 3) as H atoms, and recombine as molecular hydrogen and desorb from the permeate side (steps 4 and 5). Assuming constant diffusivity in the bulk, step 3 is rate limiting, and that the driving force for transport can be represented by the sorbed phase atomic hydrogen gradient, Fick's Law gives the steady state hydrogen flux, J_{H_2} (mol/m² s), as:

$$J_{H_2} = \frac{-DN_b}{2} \frac{dX}{dz} \quad (1)$$

where D is the hydrogen diffusivity in the bulk metal (m²/s), X is the bulk composition of hydrogen inside the membrane (mol H/mol Pd), N_b is the bulk metal Pd concentration (mol Pd/m³), and z is the spatial dimension along the thickness of the membrane. The 2

comes from the fact that there are 2 moles of H in one mole of H_2 . At steady state, the flux is independent of z , so dX/dz must also be constant (i.e., there is a linear bulk phase concentration profile). Thus Equation (1) can be re-written as:

$$J_{H_2} = \frac{D}{2L} N_b (X_f - X_p) \quad (2)$$

where X_f and X_p are the hydrogen compositions inside the membrane on the feed and permeate sides, respectively. The bulk hydrogen concentrations (X 's), in Equation (2) are related to the hydrogen pressure, P_{H_2} , by:

$$X = X_m \theta = \frac{X_m \sqrt{\frac{K_{H_2}}{RT} P_{H_2}}}{1 + \sqrt{\frac{K_{H_2}}{RT} P_{H_2}}} \quad (3)$$

where K_{H_2} is the adsorption equilibrium constant and θ is the fractional surface coverage of hydrogen. Assuming diffusion of atomic hydrogen through bulk metal to be the slowest step in the process and is considered to be rate limiting as per the Fickian diffusion, the broader steady state hydrogen permeation flux; J_{H_2} ($\text{mol}/\text{m}^2 \text{ s}$), through palladium membranes [22,56–58] can be obtained by substituting Equation (3) into (2) as follows:

$$J_{H_2} = \frac{DN_b}{2L} \left(\frac{X_m \sqrt{\frac{K_{H_2}}{RT} P_{H_2,f}}}{1 + \sqrt{\frac{K_{H_2}}{RT} P_{H_2,f}}} - \frac{X_m \sqrt{\frac{K_{H_2}}{RT} P_{H_2,p}}}{1 + \sqrt{\frac{K_{H_2}}{RT} P_{H_2,p}}} \right) \quad (4)$$

where D is the diffusion coefficient (m^2/s), L is the membrane thickness (m), K_{H_2} is the adsorption equilibrium constants on feed or permeate side (mol/m^3), and $P_{H_2,f}$ and $P_{H_2,p}$ are the feed and permeate side partial pressures of H_2 (Pa), respectively.

In order to obtain the above equation, the following assumptions were employed:

- Diffusion of H through Pd metal is rate limiting (for membrane thickness $\geq 10 \mu\text{m}$);
- Surface coverage of H at both the feed and permeate sides of the membrane is in equilibrium with the respective fluid phases;
- There is no concentration gradient at feed side (i.e., from bulk feed to membrane surface);
- Constant diffusion coefficient in Pd, i.e., $D \neq f(P_{H_2})$;
- Linear H in metal phase concentration profile, i.e., Fick's Law can be applied;
- No species other than H on surface—either adsorbed molecules or contaminants, i.e., palladium sites are not blocked and hence the effective area for permeation is the same throughout the process.

Furthermore, by assuming weak adsorption on surface, at low pressure and high temperature, we can get

$$\sqrt{\frac{K_{H_2}}{RT} P_{H_2}} \ll 1$$

Moreover, if the adsorption equilibrium constant is assumed to be the same on both sides of the membrane, then the expression of Equation (4) can be simplified in the Sieverts' Law format as follows

$$J_{H_2} = \frac{Q_{H_2}}{L} (P_{H_2,f}^{0.5} - P_{H_2,p}^{0.5}) \quad (5)$$

where Q_{H_2} is the permeability of H_2 through membrane material ($\text{mol}/\text{m s Pa}^{0.5}$), and, if Equation (4) is compared with Equation (5), then permeability can be expressed as

$$Q_{H_2} = \frac{DN_b X_m}{2} \sqrt{\frac{K_{H_2}}{RT}} \quad (6)$$

However, permeability is typically expressed in terms of diffusivity (D) and solubility (S), as per equation: $Q_{H_2} = DS$, therefore, considering Equation (6) and the latter definition the solubility (S) can be expressed as

$$S = \frac{N_b X_m}{2} \sqrt{\frac{K_{H_2}}{RT}} \quad (7)$$

Then, "Sieverts' constant", K_s , ($\text{Pa}^{0.5}$) as defined by Shu et al. [45,58], can be related to the adsorption equilibrium constant (K_{H_2}) reported in this study in Equations (4) and (5) as follows:

$$\frac{1}{K_s} = \sqrt{\frac{K_{H_2}}{RT}} \quad (8)$$

The Sieverts' constant can also be theoretically calculated at a given temperature from the correlation (16) below, where ΔH_H^0 and ΔS_H^0 stand for the standards enthalpy and entropy for atomic hydrogen and it is obtained from the literature.

$$K_s = 76.8 \exp\left(\frac{\Delta H_H^0}{RT} - \frac{\Delta S_H^0}{R}\right) \quad (9)$$

Additionally the "constant diffusivity", D (m^2/s), was calculated by employment of Equation (10) in which $E_D = 4.5 \text{ E}-7 \text{ m}^2/\text{s}$ and $D_o = 24.1 \text{ kJ/mol}$ (as given by Birnbaum and Wert [59]).

$$D = D_o e^{-E_D/RT} \quad (10)$$

When concentration polarization occurs, a layer adjacent to the surface at feed side is formed and hence hydrogen must initially diffuse through the boundary layer before reaching the membrane surface. Assuming a simple model where hydrogen is diffusing through a stagnant film of helium and if the diffusivity is assumed constant then, the steady state flux of molecular hydrogen through the boundary layer, $J_{H_2, BL}$ ($\text{mol}/\text{m}^2 \cdot \text{s}$), can be described as follows [60]:

$$J_{H_2, BL} = \frac{-D_{H_2, He} P_f}{RT\sigma} (y_{H_2, s} - y_{H_2, f}) \quad (11)$$

where $D_{H_2, He}$ is the diffusivity of H_2 in the feed mixture (m^2/s), σ is the boundary layer thickness (m), P_f is the feed pressure (Pa), and $y_{H_2, s}$ and $y_{H_2, f}$ are the H_2 mole fractions at the surface and in the bulk feed, respectively. Figure 3 shows the different layers through which hydrogen must penetrate through when, for example, a mixture feed of H_2/He is introduced and hydrogen is only permeated through the membrane material. In this figure, F_f , F_p , and F_R are total molar flow rates (in mol/s) at feed, permeate, and retentate sides, respectively. The figure reflects the hydrogen molecule concentration or partial pressure distribution and helium is not shown but the boundary layer is the layer of stagnant helium limiting the hydrogen transport in the membrane.

The concentration polarization was experimentally analyzed; however, the validity of Sieverts' Law was examined using Sieverts' Law but the pressure exponent (n) to be unknown, i.e., an empirical fit parameter, as expressed in Equation (12) below

$$J_{H_2} = \frac{Q_{H_2}}{L} (P_{H_2, f}^n - P_{H_2, p}^n) \quad (12)$$

The strong adsorption effect as well as the high temperature effect were theoretically evaluated using Equations (4), (6)–(10), and (12).

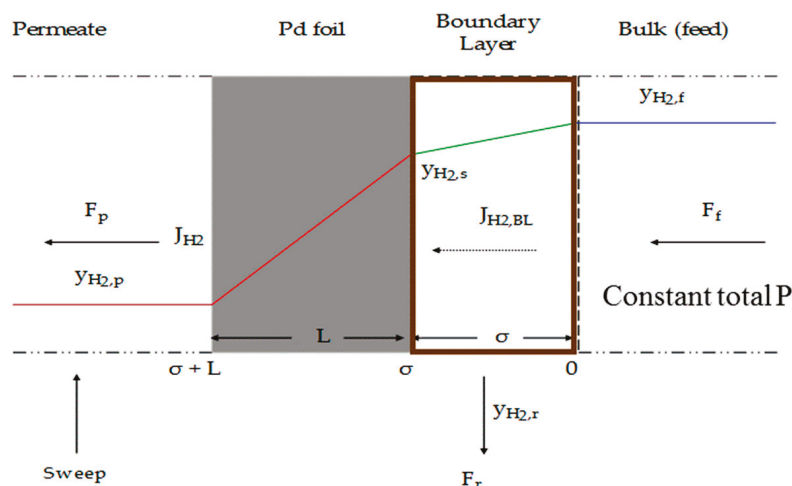


Figure 3. Schematic diagram showing concentration polarization in mixed feed.

3. Materials and Methods

3.1. Materials

Palladium foils (25 μm thick and 99.9% purity) and palladium-silver foils (75:25 wt%, 25 μm thick and 99.9% purity) were provided by Alfa Aesar (Haverhill, MA, USA). The foils were mounted in stainless steel module to be introduced in the following section. Kalrez o-rings of 45.14 ± 0.46 O.D. and 42.52 ± 0.38 mm I.D, which lose its structural integrity at 589 K, was used to seal the module. Ultra-high purity (grade 5) of 99.999% hydrogen and pure helium (grade 5) with purity of 99.999% were provided from General Air (Exton, PA, USA). Helium was used as a leak detector, inert gas, and diluent in the mixed feed gas.

3.2. Methods

3.2.1. Membrane Module Design

A membrane module was designed to insure high contact surface area and hence enhanced simulate of the realistic operating conditions. The module and inlet/outlet system were designed to fit a commercial filtration flange from Millipore with one port on each side, as illustrated in Figure 4.

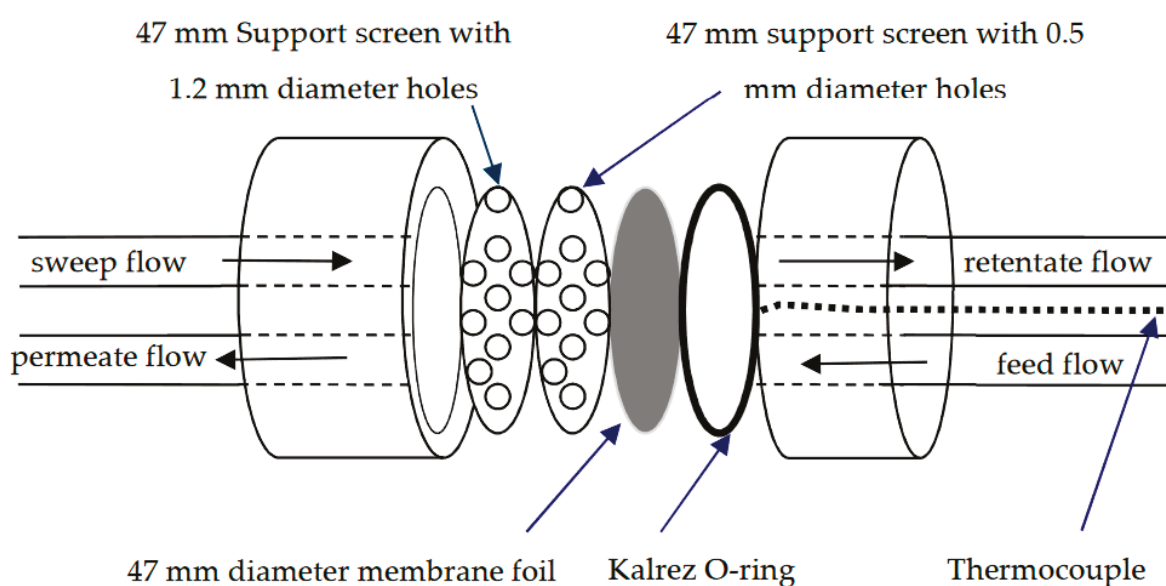


Figure 4. Schematic diagram of the used membrane module.

The module has an outer diameter of 80 mm and an inner diameter of 47 mm. It can handle a maximum inlet pressure of up to 2.0 MPa and a maximum pressure drop across the flange of 355 kPa. The measurements were typically made with feed pressures of 101–214 kPa and pressure drops range 17–121 kPa. The module has two back pressure support screens with 0.5 mm and 1.5 mm diameter holes. The 45.14 ± 0.46 O.D. and 42.52 ± 0.38 mm I.D. Kalrez o-ring was used to seal the foil to the feed side of the module, and on the permeate side, the foil seals directly to the finer support screen. The effective inner diameter of the Kalrez o-ring was estimated to be ~ 40 mm. This matches the O.D. of the screen part of the finer support. Accordingly, a calculated permeation area of 12.57 cm^2 was used for flux calculations.

The extent of mixing inside the module was characterized in a side experiment. The spreading of the peaks when the flow goes through the module indicates that mixing occurs in the module, and the composition inside the module on the feed side could assumed to be equal to the retentate composition rather than the feed composition.

3.2.2. Membrane Foil Pretreatment

All Pd-based foils, used in this study, were rinsed with acetone and then placed in stagnant air environment inside a GC-8A oven (Shimadzu, Kyoto, Japan) and then activated, *ex situ*, at 673 K and ambient pressure for one hour. Once the foil was mounted in the holder, the module was purged with inert gas to remove any air inside before the run. The inert gas continued to flow while the module was heated to the required temperature, and hence the foil was also activated *in situ* in a flowing inert gas, from room temperature to the experiment temperature (i.e., a value of 473, 523, or 573 K).

3.2.3. Experimental Setup

The used apparatus in H_2 permeation studies is shown in Figure 5. It mainly consists of a membrane holder, gas cylinders, Brooks mass flow controllers (model 5850E, AK Ruurlo, The Netherlands), a (1–10–100 mL) bubble flow meter from Hewlett-Packard (Palo Alto, CA, USA), a flow system with Swagelok G.I. 60-psi range pressure gauges (Solon, OH, USA) two thermocouples from Omega (model HH21 type J, Norwalk, CT, USA), and a Prisma Quadrupole Mass Spectrometer model QMS 200 M2, purchased from Pfeiffer Vacuum (Wetzla, Germany). The membrane module was heated inside a GC-8A type gas chromatography oven (provided by GOW-MAC Instrument Company, Bethlehem, PA, USA) and the feed side pressures were established using a 0–100 psig (0–689 kPa) Swagelok KBP series diaphragm-sensing back pressure regulator (Cleveland, OH, USA). The feed and permeate pressures were measured with a 0–100 psia (0–689 kPa) CMM-121977 HEISE pressure gauge (Stratford, CT, USA). An in-line static mixer from Koflo (model 3/8-40c-4-6-2, Cary, IL, USA) was used to introduce the desired mixtures at feed side from pure gas cylinders of hydrogen and helium. All valves were supplied by Swagelok (Solon, OH, USA).

Hydrogen permeation through Pd and Pd-25% Ag foils was developed in the Millipore membrane module in a flexible set up with or without introducing a sweep gas to carry the permeated hydrogen either to a mass spectrometer for analysis or to the bubble flowmeter for measuring its flow rate, as indicated in Figure 5. The membrane holder, as earlier mentioned, has two inlets and two outlets that allow the flow across the feed and permeate surfaces. Helium was used to purge the system prior to permeation measurements, and also to sweep permeated hydrogen in some cases. The foils were 25 μm thick with 12.57 cm^2 effective permeation area. The foil was activated (pretreated) and then mounted in the module. The helium purged air from the system and the module was heated to the run temperature, then the feed mixture was introduced to the module at the feed side to start the permeation experiments. Hydrogen permeation fluxes from mixture feeds were measured in the temperature range of 473–573 K and feed pressure range of ambient to 214 kPa for a helium mole percentage as low as 5% and as high as 83%, binary feeds. The feed flow rate was varied from 114 sccm to 485 sccm. Two foils of

palladium (Pd-1 and Pd-2) and one foil of palladium-silver alloy (75% Pd-25% Ag foil) were used to obtain the results of this work.

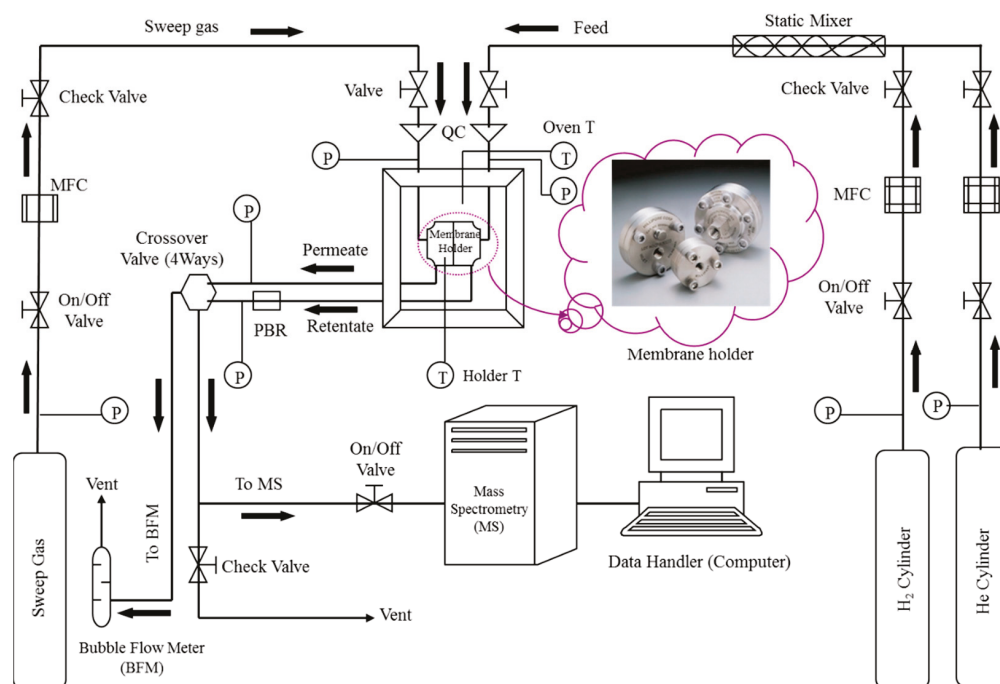


Figure 5. Schematic diagram of the experimental apparatus.

3.2.4. Theoretical Calculations

In this part of the study, the impact of various operating conditions on (n) was theoretically assessed. The modelling used Equations (4) throughout (12) to quantify the impact. To determine the effect of strong adsorption (high pressure limit) on ' n ', hydrogen fluxes (J_{H_2}) were calculated by use of Equation (4) at various feed pressures ($P_{H_2,f}$) ranged from 1 to 136 atm, while permeate pressure was maintained at 1 atm. These calculated fluxes (J_{H_2}) were then substituted into Equation (12) using same operating conditions to calculate ' n ' values as an empirical fit parameter. Similarly, the weak adsorption effect was modelled in the temperature range of 273–1273 K

4. Results and Discussion

The experimental studies analyzed hydrogen permeation fluxes from a mixed feed through two Pd (i.e., Pd-1 and Pd-2) and one Pd-Ag alloy 25 μm -thick foils at different operating conditions. The experimental studies on Pd-1 foil were achieved at an average temperature of 523 K to conceptually prove the effect of impurities and the driving force on mixed feed permeability; while for Pd-2 and Pd-Ag foils the mixed feed permeation fluxes were measured in the anticipated temperature range of 473–573 K. Additionally, the effect of strong adsorption (high pressure) and weak adsorption (high temperature) was also theoretically examined to verify the validity of Sieverts' Law assumptions, and to analyze the realistic literature values of (n).

4.1. Permeability of H_2 through Pure Palladium Foils

Two palladium foils (named Pd-1 and Pd-2) were used to study the effect of mixed feeds on hydrogen permeation. These foils had an effective permeation area of 12.57 cm^2 and were activated as described in Section 3.

4.1.1. Palladium Foil Pd-1

The Pd-1 foil was mainly used to isothermally assess the effect of hydrogen partial pressure drop, the helium composition, and the feed flow rate on the degree of con-

centration polarization in mixed feeds permeation, at 523 K. A description of Pd-1 foil permeation operating conditions and the measurements are reported below (Table S1). Hydrogen fluxes from a 95% H₂-5% He feed mixture at hydrogen partial pressure drops of 21, 62, and 117 kPa ($P_{H_2,f}$ basis) were normalized by the corresponding pure hydrogen fluxes through Pd-1 which were measured at similar conditions. For a leaner feed mixture (70% H₂-30% He), the normalized H₂ fluxes were calculated for a fixed hydrogen partial pressure drop of 62 kPa while varying the feed flow rate. Helium and hydrogen flows were adjusted to maintain the required constant hydrogen composition. The results are presented in Figure 6a for 5% He impurities in the feed while Figure 6b is for 30% He in feed.

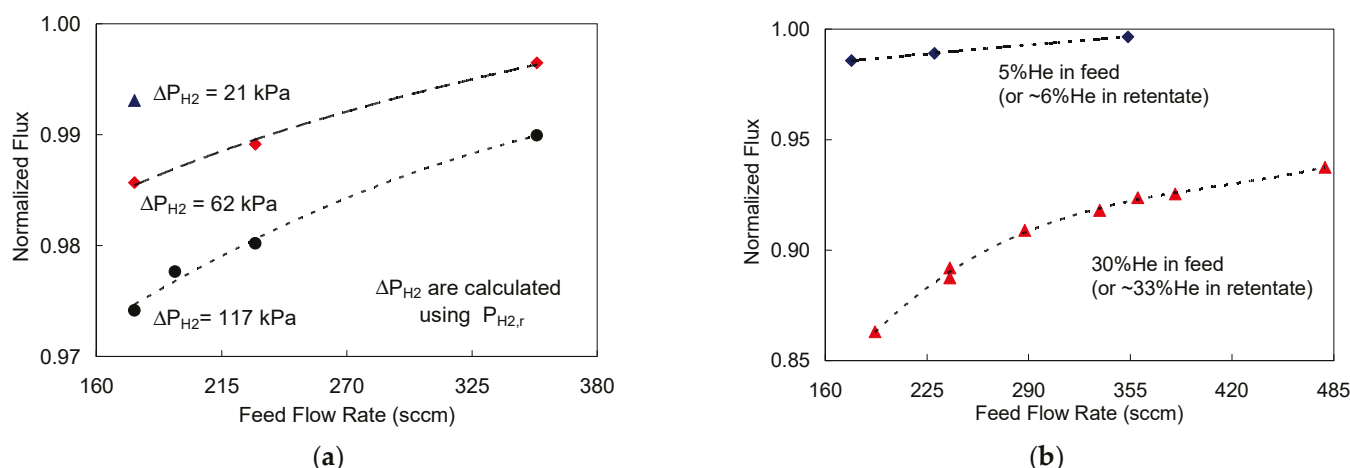


Figure 6. Hydrogen permeation fluxes through Pd-1 membrane foil at 523 K as a function of hydrogen pressure drop and feed flow rate: (a) for a 5% He feed stream with ΔP_{H_2} of 21 kPa (▲), 62 kPa (◆), and 117 kPa (●); (b) for a 30% He feed stream (▲) compared to 5% He feed stream (◆) with $\Delta P_{H_2} = 58$ kPa and $P_{H_2,f} = 152$ kPa.

The hydrogen fluxes for the 30% He were lower than those for the 5% He feed because of the stronger concentration polarization effect in the more dilute feed case, as expected [61]. Moreover, at feed flow rate of 180 sccm, the flux for 30% He feed was $\approx 12\%$ lower than that of 5% He feed; while at higher feed flow rate of 355 sccm the percentage was cut in half (i.e., 6%), as can be observed from Figure 6b. The helium mole% in the retentate stream was calculated to be about 33% when $\Delta P_{H_2} \approx 58$ kPa. As feed flow rate increased, the flux approached the pure hydrogen feed as the effect of concentration polarization decreased [17]. This behavior is concurred by the detailed results of 5% He in Figure 6a, at different pressure drops and feed flow rates.

Furthermore, hydrogen permeation from mixture feeds was also measured at 523 K maintaining ambient pressure on both sides of the membrane holder (feed and permeate). In this case, helium was used as a diluent in the feed and as a sweep on the permeate side. The helium sweep was maintained at 181 sccm, and on the feed side the helium composition was adjusted to vary from 8 to 83%. As shown in Figure 7, the H₂ fluxes with the mixture feeds did not vary linearly with $(P_{H_2,f}^{0.5} - P_{H_2,p}^{0.5})$ as predicted by Sieverts' Law.

To get a linear plot of hydrogen flux vs. $(P_{H_2,f}^n - P_{H_2,p}^n)$ n value was empirically found to be close to 1 using feed compositions in the driving force and around 0.62 using retentate compositions in the driving force indicating the gap in hydrogen partial pressure between the bulk and the feed side membrane surface. Normally H₂ permeation in the case of pure feeds is controlled by the feed and permeate pressures which are the same in bulk and close to the surface of the membrane, while in the case of mixture feeds, the more the He, or the non-permeable impurities in the feed, the greater the pressure drop in the gas film and accordingly lower driving force for hydrogen permeation [62].

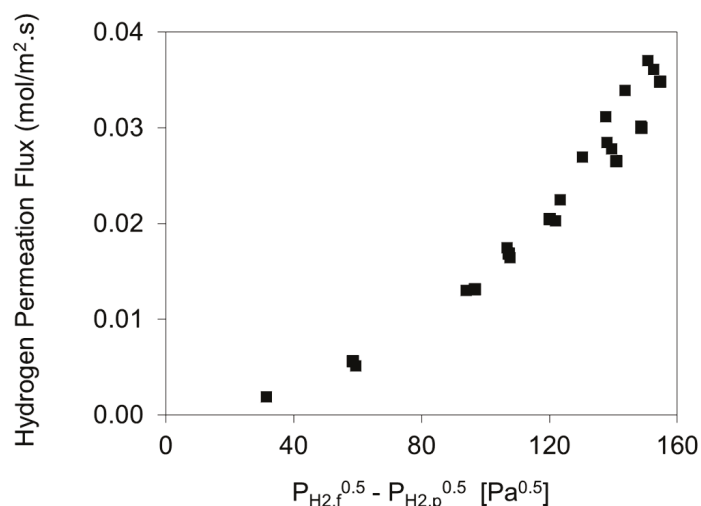


Figure 7. Mixed feed permeation through Pd-1 at 523 K for 8% to 83% He in feed balanced with hydrogen. Both sides of holder were at ambient pressure and helium used as sweep gas. Experimental runs were repeated as represented by the overlapped points.

4.1.2. Palladium Foil Pd-2

Table 1 summarizes the operating conditions of Pd-2 foil experiments for the permeation of 13.5% He in H₂ mixed feed gas. The fluxes were measured at several temperatures and retentate-based hydrogen partial pressure drops while pressure at permeate side was kept as ambient pressure. The 0.5 power dependence of the fluxes are presented in Figure 8.

Table 1. Operation conditions for H₂ in 25 µm thick Pd-2 membrane foil permeability studies.

Temperature (K)	Partial Pressure Drop (kPa)	Feed Mixture % He in H ₂	Feed Flow Rate (sccm)
473, 523, 573	~29, 40, 55, 64, 79	~13.5%	114

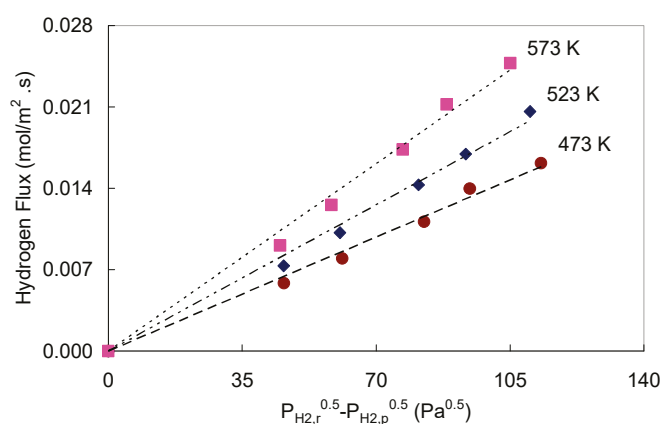


Figure 8. Hydrogen permeation fluxes, from a 13.5% He balanced with H₂, through Pd-2 foil in the temperature range of 473–573 K and $\Delta P_{H2,r}$ of ~29, 40, 55, 64, and 79 kPa.

Clearly, the permeation did not follow Sieverts' law as concentration polarization in the feed again affected the flux [30]. The helium composition in retentate varied from ~16.4 to 20.1 mol% as the pressure drop increased, at feed flow rate of 114 sccm; suggesting a more severe CP effect as more hydrogen gas permeated through the foil. To get these data to appear linear on a plot of flux vs. $(P_{H2,r}^n - P_{H2,p}^n)$, n must be about 0.9, as an average value for the three temperatures. In this case, the activation energy

for permeation determined using the Q values estimated simultaneously with n using expression (12) at various temperatures and estimated to be 8.12 kJ/mol. This value is less than the activation energy for pure hydrogen permeation through Pd-2, by $\approx 43\%$. The pre-exponential factor was $1.40 \text{ E-}10 \text{ mol/m.s.Pa}^{0.9}$, which as expected is also lower than that estimated for pure hydrogen permeation [26]. This illustrates that using Equation (12) when concentration polarization limits the permeation leads to under estimate of the permeability parameters.

4.2. Permeability of H_2 through Palladium–Silver Foils

To verify the findings obtained for Pd-1 and Pd-2 foils, the hydrogen permeation experiments were repeated from a comparable He in H_2 mixed feeds through 25 μm thick-75% Pd-25% Ag foil (called Pd-Ag) at the operating conditions listed in Table 2. Hydrogen fluxes were obtained by adjusting the helium gas flow rate in the feed (i.e., increase or decrease). The experiments were repeated at different temperatures of 473, 523, and 573 K.

Table 2. Operation conditions for 25 μm -thick (75–25%) Pd-Ag membrane foil.

Temperature (K)	Feed Mixture % He in H_2	Feed Flow Rate (sccm)	Feed Pressure (kPa)	H_2 Feed Flow Rate (sccm)	Permeate Pressure (kPa)
473, 523, 573	10–57%	15–172	214	129	93

In this study, it was observed that after each increase in helium flow rate in the feed, hydrogen flux at a given pressure was slowly decreasing. After each decrease in helium flow rate, the flux at a given pressure was slowly increasing. The steady state flux which is close to the average value of these two limits at a given pressure were used in the analysis. This method was used at all temperatures and H_2/He compositions. The pressure dependence of the hydrogen fluxes, which clearly deviates from the 0.5-power Sieverts' law, is shown in Figure 9a; where the partial pressure of H_2 on the feed side was used assuming uniform composition.

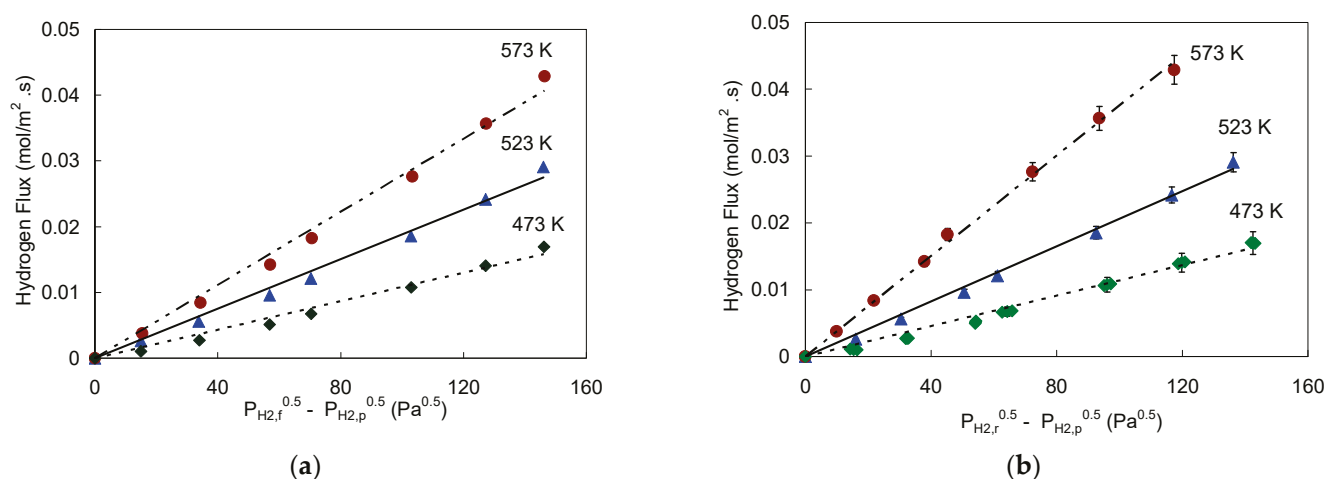


Figure 9. Hydrogen fluxes from a mixture of H_2/He through Pd-Ag foil at 473, 523, and 573 K at $P_f = 214 \text{ kPa}$ and $P_p = 93 \text{ kPa}$: (a) considering hydrogen partial pressure of the bulk feed ($P_{\text{H}_2,\text{f}}$); (b) assuming the hydrogen partial pressure in the retentate ($P_{\text{H}_2,\text{r}}$) for the composition. The straight lines to represent the best fit of Sieverts' law if assumptions are valid.

While in Figure 9b, the flux vs. $(P_{\text{H}_2,\text{r}}^{0.5} - P_{\text{H}_2,\text{p}}^{0.5})$ was plotted using the retentate composition; a less dramatic deviation from Sieverts' law was observed. The best fit of the data, presented in Figure 9a,b, was obtained when $n \sim 1.4$, when the feed composition was used, and $n \sim 1.0$, when the retentate composition was used, respectively. This

suggests that diffusion of hydrogen through the bulk metal was not the rate limiting step in these measurements [63]. Using Equation (12) with the retentate composition as the feed composition and $n = 1$, an activation energy of 21.37 kJ/mol and a pre-exponential factor (Q_0) of 2.53 E-10 mol/m.s.Pa were obtained. The values are not expected to be same as to those obtained from experiments in which Sieverts' Law is valid [23]. Interestingly gas phase diffusion weakly depends on temperature compared to activated diffusion through membranes [62], accordingly the activation energy for these measurements is expected to be lower than that through the Pd-Ag membrane. Indeed, the estimated activation energy for transport through a boundary layer and then through the Pd-Ag membrane was found to be $\approx 18\%$ lower than that for pure hydrogen transport alone through the same foil in the same temperature range. The values were obtained from the Arrhenius Plot using the results of Figure 9b.

4.3. Analyzing Sieverts' Law Assumptions for the Mixed Feeds Permeation in Pd and Pd-Ag Foils

As of the results presented earlier, it clear that hydrogen permeation from mixture feeds of hydrogen/helium through the Pd and Pd-Ag membrane foils in the current study deviated from Sievert's Law at the conditions tabulated earlier. The comparative results of Pd-2 and Pd-Ag foils at 523 K were generated in Figure 10. As expected, H_2 fluxes in Pd-Ag were higher than those of Pd-2 foil but, as previously indicated, both do not follow Sieverts' 0.5-power law (Figure 10a). To better understand the concentration polarization behavior in the two foils, the normalized fluxes were considered in Figure 10b. H_2 fluxes in Pd-2 foil were obtained by varying the feed pressure and maintaining the total feed flowrate at approximately 152 sccm while fluxes of Pd-Ag foil were obtained by adding more helium in the feed at constant total feed pressure of 214 kPa. Accordingly, for Pd-2 foil the increase in the feed pressure increased the driving force for hydrogen permeation, since the permeation process is fast a fluid phase layer was developed on the surface limiting the hydrogen flux and possibly led to surface saturation. On the other hand, for Pd-Ag foil, the added helium increased the formation of fluid phase layer but with relatively increased total feed flow rate, the CP effect was slightly minimized, and hence this explains the increase in the gap in Figure 10a as hydrogen pressure difference increased. These remarks support the results obtained for Pd-1 foil and illustrated in Figure 6.

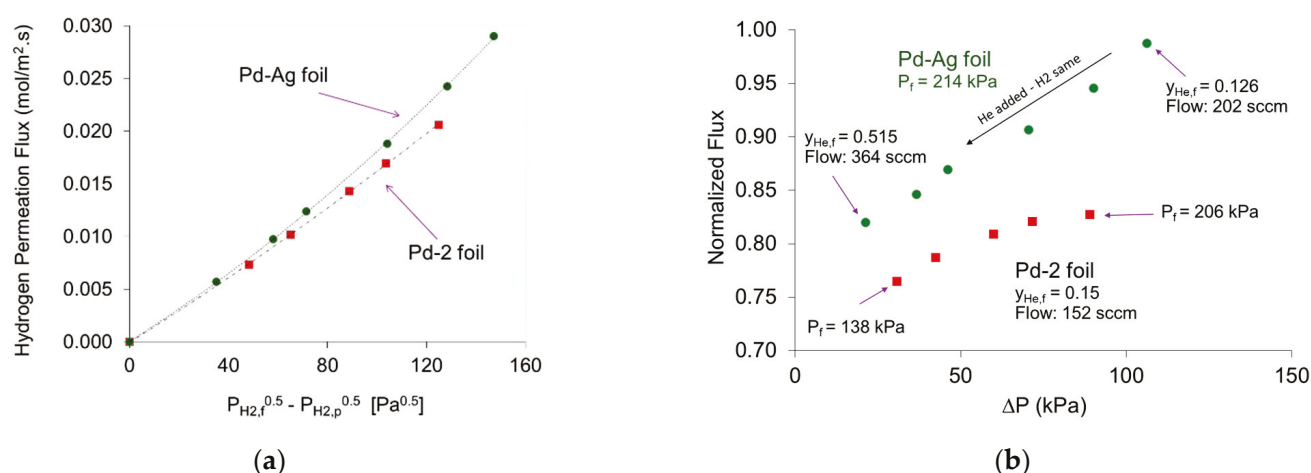


Figure 10. Hydrogen fluxes from a mixture of H_2/He at 523 K through Pd-2 (in red symbols) and Pd-Ag (in green symbols) foils (a) as a function of $P_{H_2}^{0.5}$ (Sieverts' Law) for helium compositions of 0.15 and (0.126 to 0.515), respectively (b) as a normalized flux versus hydrogen pressure drop. Permeate pressure was 93 kPa.

Selective and fast hydrogen depletion through Pd-based membrane foils leads to accumulation of helium near the Pd surface, which causes a concentration gradient across

a boundary layer in the feed [61]. Due to this phenomena, the partial pressure of hydrogen in the bulk feed is not equal to the partial pressure of hydrogen at the surface, which is a violation of one assumption in Sievert Law [17]. Hydrogen diffusion through the system can therefore be perfectly limited by the hydrogen diffusion through the boundary layer (fluid phase mass transfer) rather than diffusion through the foil itself, which would normally lead to a linear dependence (i.e., $n = 1$) of flux on hydrogen partial pressures rather than the 0.5 exponent dependence of Sieverts' law [23]. If both resistances are important, the exponent on the partial pressures can be between 0.5 and 1 [23]. Concentration polarization obviously also lowers the flux in addition to changing the pressure dependence of the flux, and improper analysis of fluxes measured under conditions where concentration polarization is completely or partly rate limiting leads to underestimates of the membrane permeability and its activation energy [17]. Furthermore, increasing the feed flow rate decreases the effect of concentration polarization. Considering the influence of the flow rate at the exit of the retentate side on H_2 flux, a higher flow rate means more H_2 being sent into the membrane surface, sweeping the other impurities and rendering a thinner H_2 boundary layer along the membrane surface. This results in a larger H_2 concentration gradient on the surface and thereby intensifying H_2 flux [63]. Hence, the total feed flow rate should be considered when comparing hydrogen flux from feed mixture results, which is not necessary when comparing pure hydrogen permeation fluxes [13]. At higher partial pressure driving forces across the foil, concentration polarization is also more severe as would be expected.

5. Mathematical Modeling

Equations (4) and (12) were mainly used to model and to independently assess the strong and weak adsorption on validity of 0.5-power Sieverts' law for the pure H_2 permeation through 25 μm thick Pd foils. All parameters which were used in the model calculations are reported in Table 3.

Table 3. Parameter values used in model calculations.

Parameter	Value	Units	References
Q_0	9.29×10^{-8}	$\text{mol/m s Pa}^{0.5}$	(Current study)
E_p	11.7	kJ/mol	(Current study)
D_0	4.5×10^{-7}	m^2/s	Birnbaum and Wert(1972) [59]
E_D	24.1	kJ/mol	Birnbaum and Wert (1972) [59]
ΔH_H^0	−8.4	kJ/mol	Holleck (1991) [64]
ΔS_H^0	−48.7	J/mol K	Holleck (1991) [64]
N_b	1.13×10^5	mol Pd/ m^3	Ward and Dao (1999) [22]
X_m	0.65	mol H/mol Pd	Smirnov and Gol'tsov(1988) [65]
R	8.314	J/mol K	(Gas constant)

5.1. Effect of High Pressure Limits (Strong Adsorption)

The strong adsorption effect on hydrogen permeation and consequently on the power exponent (n) was assessed at 523 K for pure H_2 permeation through Pd foil. The feed pressure ($P_{H_2,f}$) was varied from 101 to 13,736 kPa (i.e., 1 to 136 atm) with permeate side at ambient pressure ($P_{H_2,p}$). The results are presented in Figure 11. Additional temperature results in the range of 473–573 K are available in the supplementary information (Table S1).

The modelling results showed (n) values deviated from the 0.5 power. Clearly in Figure 11, as the P_{H_2} increased the pressure exponent (n) decreased below 0.5. Theoretically, if P_{H_2} approaches the infinity (∞) then the membrane will be saturated and hence n will approach zero, suggesting a permeation rate to be independent of P_{H_2} . Therefore, the very strong adsorption in the case of a very high applied pressure, hypothetically indicate that the assumption $\sqrt{\frac{KP}{RT}} \ll 1$ in deriving the Sieverts' law is invalid.

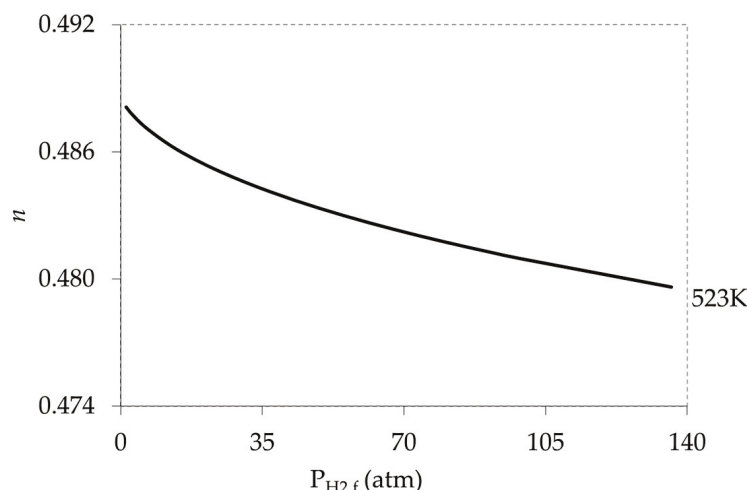


Figure 11. Modeling the effect of strong adsorption on pressure exponent (n) at 523 K.

5.2. Effect of Weak Adsorption (High Temperature Limits) on Pressure Exponent (n)

Similarly, the effect of weak adsorption (high temperature) was modeled by varying the temperature from 298 to 1273 K. Three different feed pressures were chosen in the model, i.e., 1.36, 30.62, and 68.08 atm. The permeate side was kept at ambient conditions. The temperature dependency, as per model used, is reported in Figure 12. An increase of absolute temperature by ≈ 3 times resulted in an increase of n values by 7% towards the 0.5 value. The weak adsorption supports the Sieverts' law validity because it validates the assumption $\sqrt{\frac{KP}{RT}} \ll 1$.

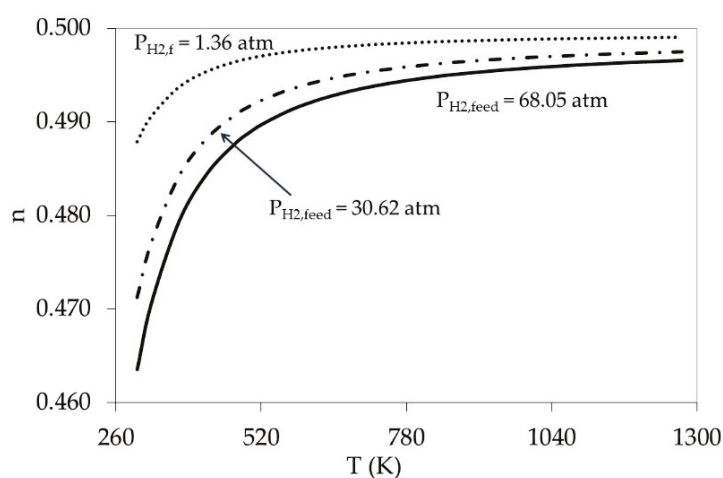


Figure 12. Modeling the effect of weak adsorption (high temperature) on hydrogen permeation rate and the corresponding (n) value for hydrogen partial pressures in the range of 1.36–30.62 atm.

5.3. Combining the Effect of Pressure and Temperature in the Model

All results in Figures 11 and 12 were obtained assuming low pressure at permeate side, and also individually addressed the effect of each parameter on (n). For example, an increase in feed pressure by ≈ 130 atm caused a decline of (n) value by only 2%. While a decrease of the temperature by 3 times lowered the (n) value by 7%. Furthermore, a simultaneous increase of pressure accompanied by a decrease of temperature resulted in a 30–50% more effect on (n) because the assumption $\sqrt{\frac{KP}{RT}} \ll 1$ is strongly not valid.

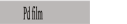
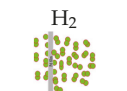
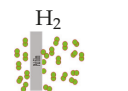
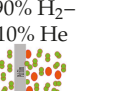
6. Explaining the Literature (n) Values and the Future Work Direction

The effect of high sorption coverage, i.e., high pressure or high adsorption equilibrium constant, as well as the concentration polarization were previously investigated.

Concentration polarization resulted in pressure exponent (n) values between 0.5 and 1.0, a high sorption theoretically assessed and produced (n) values below 0.5. These effects were independently addressed and their impacts were quantified. If combined, the degree of the deviation from Sieverts' law will probably depend on the contribution of each step in the permeation process.

Table 4 summarizes the membranes features and the operating conditions for some realistic studies, in which (n) was treated as an empirical fit parameter and its value varied from 0.5 to 1.41, as follows: (i) supported or non-supported Pd as thin as 0.5 μm and as thick as 1000 μm , (ii) temperature range of 623–1219 K, (iii) pure feed gas or mixed feed with up to 80% He, (iv) feed pressure in the range of ≈ 1 –27 atm, and (v) permeate pressure either as vacuum or 1 atm (sweep gas). The (n) values were qualitatively interpreted and possible explanations were provided according to current study outcomes.

Table 4. Literature pressure exponent (n) values for hydrogen permeation through supported and unsupported Pd membranes from pure and mixture feeds.

References Parameters	Hurlbert and Konecny [66]	Katsuta et al. [67]	Morreale et al. [24]	Gielens et al. [25]	Gielens et al. [25]	Chen et al. [61]	Chen et al. [61]
L (μm)	10–150 no support 	940 no support 	1000 no support 	0.9 no support 	0.5 with support 	6.93 Tubular 	6.63 Tubular 
T (K)	623–773	769–1219	623–1173	623–873	623–873	623	623
Feed gas			90% H ₂ – 10% He 	20% H ₂ – 80% He 	20% H ₂ – 80% He 	H ₂	75% H ₂ – 25% N ₂
P _{total,f} (kPa)	101–710	101	101–2760	101–505	101–505	101–202	303–506
P _{H₂,f} (kPa)	101–710	101	91–2480	20–101	20–101	101–202	303–506
P _{total,p} (kPa)	Vacuum	Vacuum	118	101	101	101	101
Permeate condition	Vacuum	Vacuum	Ar sweep	N ₂ sweep	N ₂ sweep	N ₂ sweep	N ₂ sweep
n	0.68	0.5	0.62	0.5–1.04 **	0.58–1.41 **	0.5	1.0
Possible justification of (n)	L-Thick Pd *** Pure H ₂ ($n \approx 0.5$), high P ($n < 0.5$), High T ($n \sim 0.5$), high ΔP_{H_2} desorption rate limiting ($n \approx 1$) → Avg. (n) = 0.7	H-Thick Pd Pure H ₂ ($n = 0.5$), (low P and high T) ($n = 0.5$), low ΔP_{H_2} → Sieverts' Law ($n = 0.5$)	Thick Pd ($n = 0.5$), with lower CP * effect at feed ($n \sim 0.8$), Very high P ($n < 0.5$), high T ($n \sim 0.5$), → Avg. (n) = 0.63	Thin Pd Strong mixed effect (CP *) and sweep ($n = 1$), High T ($n \sim 0.5$), moderate P ($n \sim 0.5$), → Very thin membrane with strong CP ($n = 1$)	Thin Pd Strong mixed feed or CP * ($n = 1$), high T ($n \sim 0.5$), Viscous flow in support flux α P _{H₂} ² ($n = 2$), moderate P ($n \sim 0.5$) → Avg. (n) = 1.38	Thin Pd Pure H ₂ low P ($n = 0.5$), High T ($n = 0.5$), → Avg. ($n \sim 0.5$)	Thin Pd Strong mixed feed or CP * ($n = 1$), low P ($n = 0.5$), High T ($n = 0.5$), → mass transfer in fluid phase is the limiting step ($n \sim 1.0$)

* CP is an abbreviation for concentration polarization. ** Upper limit was evaluated. *** L-Thick Pd means relatively thick Pd and H-Thick Pd refers to a very thick film.

Hurlbert and Konecny [66] reported an (n) value of 0.68 for pure H₂ permeation through 10–150 μm (relatively) thick Pd membranes with relatively high P_{H₂,f} = 7 atm and T > 623 K and permeate side at vacuum. This value can be justified by the combined effect of thick membrane ($n = 0.5$), high T ($n \rightarrow 0.5$), high P_f ($n < 0.5$), and desorption limiting ($n \approx 1$). Moreover, Katsuta and coworkers [67] assessed hydrogen permeation through a very thick Pd membrane at operating conditions favored the 0.5 power. Furthermore, Morreale et al. (2003) [24] investigated the mixed feed (10% He balanced with H₂) permeation for very thickness Pd in a relatively high temperature and pressure which resulted in a pressure exponent value between 0.5 and 1.0. Interestingly Gielens and

coworkers [25] conducted two studies one with support and one without, however, in both 80% He–20% H₂ mixture was introduced to a very thin palladium at relatively high temperature. For the non-supported Pd the strong concentration polarization gave $n \approx 1$, while in the supported-Pd membrane the contribution was cumulative (CP $\rightarrow n = 1$, support $\rightarrow J_{H_2, \text{support}} \propto P^2 \rightarrow n = 2$, high T $\rightarrow n = 0.5$) so n was estimated to be ~ 1.4 [68]. Most recently Chen and coworkers [61] reported exponent values of 0.5 for very thin tubular Pd membrane at relatively high temperature and moderate pressure drop. When 25% N₂ balanced with hydrogen was introduced to the system a severe CP effect was observed leading to an (n) value of 1.0, as expected.

The above qualitative analyses of n values in Table 4 clearly support the findings of this work. The values obtained by qualitative analyses were close enough to the literature-reported values. However, this study did not take into account the Pd surface contaminants [69–71] or the membrane activation [72] to physically or chemically block the surface. Nevertheless, the better understanding of the assumptions in Sieverts' Law enabled the authors to explain some of the literature values for similar conditions, such the nature of the feed gas, operating conditions, and nature of the membrane (thickness, dense or composite). Additionally, Suzuki and coworkers reviewed various methods for consistent analysis of hydrogen permeability [73].

The limited applicability of the current approach suggests to better understand the H₂ transport in the palladium-based catalytic membrane reactors and consequently the Sieverts' Law assumptions. This requires a general transport model to incorporate all possible mass transfer resistances [74], in addition to the reaction. The incorporation of general model in assessing the assumptions of Sieverts' Law and quantify the role of each effect (i.e., mixed feed, support, thickness, catalyst, T, P, etc.) The general model aims at numerically determining the pressure exponent (n) values. Figure 13 shows the possible resistances in a typical Pd-membrane reactor; as follows: (1) fluid phase mass transfer, (2) flow through support, (3) H₂ dissociative adsorption on surface, (4) H from surface to inside Pd, (5) H diffusion in Pd, (6) H from bulk to surface, (7) H atoms re-combinative desorption, (8) H atom spill-over on catalyst, (9) surface reaction, and (10) unreacted or produced H₂ flow through fluid phase mass transfer. This proposed transport maybe slightly different if hydrogenation or dehydrogenation reactions involved, or there is a need for support on both sides, or the nature and stability of the catalyst (i.e., metal segregation), and finally the shape of the module (disk, sheet, tube, hollow fiber, etc.).

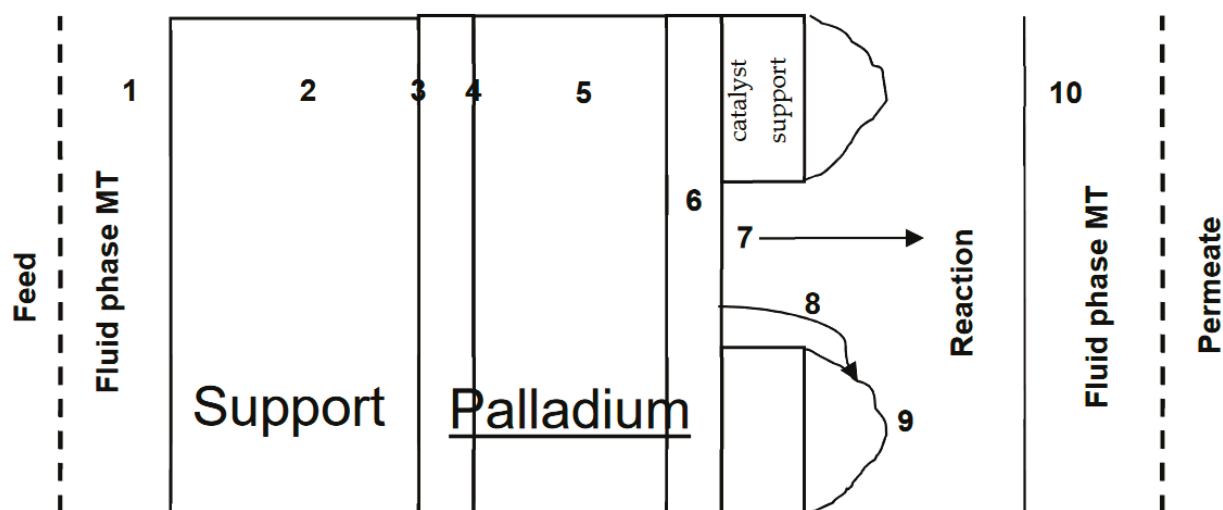


Figure 13. Schematic diagram of resistances to hydrogen transport through a catalytic Pd-based membrane reactor, with supported catalyst.

7. Conclusions

Palladium membranes can be effectively employed inside reactors, and most recently for hydrogen production from fossil fuels or from bio-wastes. The use of Sieverts' law with 0.5 exponent in such complicated system would either underestimate or overestimate the hydrogen flux. Hence, some of the assumptions used in deriving Sieverts' Law were assessed in this study, either experimentally or by means of a simple model, to describe the reported literature pressure exponent (n) in comparable studies. The assumptions of our interest are: (i) diffusion of H through Pd metal is rate limiting, (ii) there is no concentration gradient at the feed side, (iii) no species other than H₂ on surface, and (iv) weak adsorption behavior on surface. Hydrogen permeation studies from a mixture feed through Pd-1, Pd-2, and Pd-Ag foils at different temperatures and pressure drops resulted in a decline of H₂ flux suggesting formation of an impermeable gas close to the membrane surface (CP effect). The (n) value of 1.0, which was obtained from the experimental data, suggests that concentration polarization to be dominant and hence assumption (i) probably invalid. The pressure exponent (n) of 0.9 for Pd-2 foil fluxes confirms a partial contribution of mixed feed effect on the validity of assumption (i), as rate limiting step. Moreover, the Pd-1 studies stressed on importance of the feed flow rate to minimize the CP effect, a 7% increase was observed in the normalized flux for 30% He in feed when total feed flow rate was doubled. This explains that the actual driving force for the permeation is lower than the theoretical value, i.e., $P_{H_2,f} > P_{H_2,surface}$, and therefore, probably assumption (ii) in Sieverts' law is not anymore valid. Furthermore, the use of mixed feed with CP limitations may also affect the assumption (iii), as helium physically stays on the foil surface. A stronger effect of this assumption can be observed if contaminants like carbon chemically adsorbs on the surface, but in our study this was minimized or eliminated when membranes foil were ex situ activated at 673 K. Lastly, assumption (iv) was examined at high adsorption coverage, i.e., at high pressure and low temperature, using a simple model assuming Langmuir adsorption with temperature dependent adsorption equilibrium coefficient. Mathematical modelling confirmed that high pressures or low temperatures could lead to $n < 0.5$ but based on the literature values normally n is ≥ 0.5 , which may suggest that the two effects are present but marginalized with the stronger impact of the other steps. The experiments and modelling in this study offer possible reasons explaining why experimentally fit value of the exponent, n , deviate from 0.5. A more general model including concentration polarization and high adsorption coverage effects on hydrogen transport in metal-based catalytic membrane reactor was presented, accounting for the catalytic multi-layered porous support.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/membranes11100778/s1>, Figure S1: Modeling the effect of strong adsorption (high P) on pressure exponent (n) for temperature range of 473–573 K. Table S1: Operation conditions for H₂ in 25 μ m thick Pd-1 membrane foil permeability studies.

Author Contributions: Conceptualization, A.A.; methodology, A.A.; validation, A.A.; formal analysis, A.A.; investigation, A.A.; resources, T.G.; data curation, A.A.; writing—original draft preparation, A.A.; writing—review and editing, A.A. and T.G.; supervision, T.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors would like to thank: the Chemical and Biological Engineering Department at Colorado School of Mines for the facilities to conduct the experiments, Angel Abbud-Madrid for his logistic support to demonstrate the experiments at Center for Space Resources, and the Abu Dhabi National Oil Company (ADNOC) for securing the resources for the laboratory work. The authors would also like to express their appreciation to the United Arab Emirates University for the financial support and the startup grant (31N195) which supported the completion and publication of this work. The authors also thank Ameera Mohammad for her aid in manuscript formatting.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Zhou, L.; Liao, Z.; Wang, J.; Jiang, B.; Yang, Y. Hydrogen sulfide removal process embedded optimization of hydrogen network. *Int. J. Hydrogen Energy* **2012**, *37*, 18163–18174. [CrossRef]
2. Chinchén, G.; Denny, P.; Jennings, J.; Spencer, M.; Waugh, K. Synthesis of Methanol. *Appl. Catal.* **1988**, *36*, 1–65. [CrossRef]
3. Khila, Z.; Hajjaji, N.; Pons, M.-N.; Renaudin, V.; Houas, A. A comparative study on energetic and exergetic assessment of hydrogen production from bioethanol via steam reforming, partial oxidation and auto-thermal reforming processes. *Fuel Process. Technol.* **2013**, *112*, 19–27. [CrossRef]
4. Wiheeb, A.; Martunus; Helwani, Z.; Shamsudin, I.; Kim, J.; Othman, M. Pore morphological identification of hydrotalcite from nitrogen adsorption. *Chaos, Solitons Fractals* **2013**, *49*, 7–15. [CrossRef]
5. Chaubey, R.; Sahu, S.; James, O.; Maity, S. A review on development of industrial processes and emerging techniques for production of hydrogen from renewable and sustainable sources. *Renew. Sustain. Energy Rev.* **2013**, *23*, 443–462. [CrossRef]
6. Osman, A.I.; Deka, T.J.; Baruah, D.C.; Rooney, D.W. Critical challenges in biohydrogen production processes from the organic feedstocks. *Biomass-Conv. Biorefinery* **2020**, 1–19. [CrossRef]
7. Tian, H.; Li, J.; Yan, M.; Tong, Y.W.; Wang, C.-H.; Wang, X. Organic waste to biohydrogen: A critical review from technological development and environmental impact analysis perspective. *Appl. Energy* **2019**, *256*, 113961. [CrossRef]
8. Chandrasekhar, K.; Lee, Y.-J.; Lee, D.-W. Biohydrogen Production: Strategies to Improve Process Efficiency through Microbial Routes. *Int. J. Mol. Sci.* **2015**, *16*, 8266–8293. [CrossRef] [PubMed]
9. Kapoor, D.; Oberoi, A.S.; Nijhawan, P. Hydrogen Production and Subsequent Adsorption/Desorption Process within a Modified Unitized Regenerative Fuel Cell. *Process* **2019**, *7*, 238. [CrossRef]
10. Assabumrungrat, S.; Wongsakulphasatch, S.; Kim, P.L.; Rodrigues, A.E. Special Issue on “Hydrogen Production Technologies”. *Process* **2020**, *8*, 1268. [CrossRef]
11. Tashie-Lewis, B.C.; Nnabuike, S.G. Hydrogen Production, Distribution, Storage and Power Conversion in a Hydrogen Economy - A Technology Review. *Chem. Eng. J. Adv.* **2021**, *8*, 100172. [CrossRef]
12. Lan, R.; Irvine, J.; Tao, S. Ammonia and related chemicals as potential indirect hydrogen storage materials. *Int. J. Hydrogen Energy* **2012**, *37*, 1482–1494. [CrossRef]
13. Dunbar, Z.W. Hydrogen purification of synthetic water gas shift gases using microstructured palladium membranes. *J. Power Sources* **2015**, *297*, 525–533. [CrossRef]
14. Ahluwalia, R.; Hua, T.; Peng, J. On-board and Off-board performance of hydrogen storage options for light-duty vehicles. *Int. J. Hydrogen Energy* **2012**, *37*, 2891–2910. [CrossRef]
15. Lu, G.; da Costa, J.C.D.; Duke, M.; Giessler, S.; Socolow, R.; Williams, R.; Kreutz, T. Inorganic membranes for hydrogen production and purification: A critical review and perspective. *J. Colloid Interface Sci.* **2007**, *314*, 589–603. [CrossRef]
16. Sánchez, J.; Barreiro, M.; Maroño, M. Bench-scale study of separation of hydrogen from gasification gases using a palladium-based membrane reactor. *Fuel* **2014**, *116*, 894–903. [CrossRef]
17. Zhang, J.; Liu, D.; He, M.; Xu, H.; Li, W. Experimental and simulation studies on concentration polarization in H₂ enrichment by highly permeable and selective Pd membranes. *J. Membr. Sci.* **2006**, *274*, 83–91. [CrossRef]
18. Rahimpour, M.R.; Samimi, F.; Babapoor, A.; Tohidian, T.; Mohebi, S. Palladium membranes applications in reaction systems for hydrogen separation and purification: A review. *Chem. Eng. Process. Process. Intensif.* **2017**, *121*, 24–49. [CrossRef]
19. Brunetti, A.; Zito, P.F.; Giorno, L.; Drioli, E.; Barbieri, G. Membrane reactors for low temperature applications: An overview. *Chem. Eng. Process. Process. Intensif.* **2018**, *124*, 282–307. [CrossRef]
20. Di Marcoberardino, G.; Binotti, M.; Manzolini, G.; Viviente, J.L.; Arratibel, A.; Roses, L.; Gallucci, F. Achievements of European projects on membrane reactor for hydrogen production. *J. Clean. Prod.* **2017**, *161*, 1442–1450. [CrossRef]
21. Li, P.; Wang, Z.; Qiao, Z.; Liu, Y.; Cao, X.; Li, W.; Wang, J.; Wang, S. Recent developments in membranes for efficient hydrogen purification. *J. Membr. Sci.* **2015**, *495*, 130–168. [CrossRef]
22. Ward, T.L.; Dao, T. Model of hydrogen permeation behavior in palladium membranes. *J. Membr. Sci.* **1999**, *153*, 211–231. [CrossRef]
23. Caravella, A.; Hara, S.; Drioli, E.; Barbieri, G. Sieverts law pressure exponent for hydrogen permeation through Pd-based membranes: Coupled influence of non-ideal diffusion and multicomponent external mass transfer. *Int. J. Hydrogen Energy* **2013**, *38*, 16229–16244. [CrossRef]

24. Morreale, B.D.; Ciocco, M.V.; Enick, R.M.; Morsi, B.I.; Howard, B.H.; Cugini, A.V.; Rothenberger, K.S. The permeability of hydrogen in bulk palladium at elevated temperatures and pressures. *J. Membr. Sci.* **2003**, *212*, 87–97. [CrossRef]
25. Gielens, F.; Tong, H.; Vorstman, M.; Keurentjes, J. Measurement and modeling of hydrogen transport through high-flux Pd membranes. *J. Membr. Sci.* **2007**, *289*, 15–25. [CrossRef]
26. Dunbar, Z.W.; Lee, I.C. Effects of elevated temperatures and contaminated hydrogen gas mixtures on novel ultrathin palladium composite membranes. *Int. J. Hydrogen Energy* **2017**, *42*, 29310–29319. [CrossRef]
27. Hara, S.; Caravella, A.; Ishitsuka, M.; Suda, H.; Mukaida, M.; Haraya, K.; Shimano, E.; Tsuji, T. Hydrogen diffusion coefficient and mobility in palladium as a function of equilibrium pressure evaluated by permeation measurement. *J. Membr. Sci.* **2012**, *421–422*, 355–360. [CrossRef]
28. Pati, S.; Jat, R.A.; Anand, N.; Derosé, D.J.; Karn, K.; Mukerjee, S.; Parida, S. Pd-Ag-Cu dense metallic membrane for hydrogen isotope purification and recovery at low pressures. *J. Membr. Sci.* **2017**, *522*, 151–158. [CrossRef]
29. Jia, H.; Wu, P.; Zeng, G.; Colera, E.S.; Serrano, A.; Castro, G.R.; Xu, H.; Sun, C.; Goldbach, A. High-temperature stability of Pd alloy membranes containing Cu and Au. *J. Membr. Sci.* **2017**, *544*, 151–160. [CrossRef]
30. Deveau, N.; Ma, Y.H.; Datta, R. Beyond Sieverts' law: A comprehensive microkinetic model of hydrogen permeation in dense metal membranes. *J. Membr. Sci.* **2013**, *437*, 298–311. [CrossRef]
31. Caravella, A.; Hara, S.; Sun, Y.; Drioli, E.; Barbieri, G. Coupled influence of non-ideal diffusion and multilayer asymmetric porous supports on Sieverts law pressure exponent for hydrogen permeation in composite Pd-based membranes. *Int. J. Hydrogen Energy* **2014**, *39*, 2201–2214. [CrossRef]
32. Chen, Y.; Wang, J.; Flanagan, D. Fundamental of Diffusion and Dissolution. *Developing Solid Oral Dosage Forms* **2017**, 253–270. [CrossRef]
33. Flanagan, T.B.; Wang, D.; Luo, S. Thermodynamics of hydrogen absorption (desorption) in unoxidized and internally oxidized Pd-Ti alloys. *J. Alloy. Compd.* **2017**, *701*, 981–992. [CrossRef]
34. Flanagan, T.B.; Wang, D. Exponents for the Pressure Dependence of Hydrogen Permeation through Pd and Pd–Ag Alloy Membranes. *J. Phys. Chem. C* **2010**, *114*, 14482–14488. [CrossRef]
35. Hara, S.; Ishitsuka, M.; Suda, H.; Mukaida, M.; Haraya, K. Pressure-Dependent Hydrogen Permeability Extended for Metal Membranes Not Obeying the Square-Root Law. *J. Phys. Chem. B* **2009**, *113*, 9795–9801. [CrossRef] [PubMed]
36. Peters, T.; Stange, M.; Klette, H.; Bredesen, R. High pressure performance of thin Pd–23%Ag/stainless steel composite membranes in water gas shift gas mixtures; influence of dilution, mass transfer and surface effects on the hydrogen flux. *J. Membr. Sci.* **2008**, *316*, 119–127. [CrossRef]
37. Bhattacharya, S. Concentration polarization, separation factor, and Peclet number in membrane processes. *J. Membr. Sci.* **1997**, *132*, 73–90. [CrossRef]
38. Gao, H.; Lin, Y.S.; Li, A.Y.; Zhang, B. Chemical Stability and Its Improvement of Palladium-Based Metallic Membranes. *Ind. Eng. Chem. Res.* **2004**, *43*, 6920–6930. [CrossRef]
39. Chen, W.-H.; Syu, W.-Z.; Hung, C.-I. Numerical characterization on concentration polarization of hydrogen permeation in a Pd-based membrane tube. *Int. J. Hydrogen Energy* **2011**, *36*, 14734–14744. [CrossRef]
40. Lüdtke, O.; Behling, R.-D.; Ohlrogge, K. Concentration polarization in gas permeation. *J. Membr. Sci.* **1998**, *146*, 145–157. [CrossRef]
41. Mardilovich, P.P.; She, Y.; Ma, Y.H.; Rei, M.-H. Defect-free palladium membranes on porous stainless-steel support. *AIChE J.* **1998**, *44*, 310–322. [CrossRef]
42. Tong, J.; Su, L.; Haraya, K.; Suda, H. Thin Pd membrane on α -Al₂O₃ hollow fiber substrate without any interlayer by electroless plating combined with embedding Pd catalyst in polymer template. *J. Membr. Sci.* **2008**, *310*, 93–101. [CrossRef]
43. Chen, W.-H.; Chiu, I.-H. Transient dynamic of hydrogen permeation through a palladium membrane. *Int. J. Hydrogen Energy* **2009**, *34*, 2440–2448. [CrossRef]
44. Algieri, C.; Coppola, G.; Mukherjee, D.; Shammas, M.; Calabro, V.; Curcio, S.; Chakraborty, S. Catalytic Membrane Reactors: The Industrial Applications Perspective. *Catalysts* **2021**, *11*, 691. [CrossRef]
45. Al-Shammary, A.F.Y.; Caga, I.T.; Winterbottom, J.M.; Tata, A.Y.; Harris, I.R. Palladium-based diffusion membranes as catalysts in ethylene hydrogenation. *J. Chem. Technol. Biotechnol.* **1991**, *52*, 571–585. [CrossRef]
46. Unlu, D.; Hilmioglu, N.D. Pervaporation catalytic membrane reactor application over functional chitosan membrane. *J. Membr. Sci.* **2018**, *559*, 138–147. [CrossRef]
47. Chen, Y.-R.; Tsuru, T.; Kang, D.-Y. Simulation and design of catalytic membrane reactor for hydrogen production via methylcyclohexane dehydrogenation. *Int. J. Hydrogen Energy* **2017**, *42*, 26296–26307. [CrossRef]
48. Baráth, E. Hydrogen Transfer Reactions of Carbonyls, Alkynes, and Alkenes with Noble Metals in the Presence of Alcohols/Ethers and Amines as Hydrogen Donors. *Catalysts* **2018**, *8*, 671. [CrossRef]
49. Fellechner, O.; Blatkiwicz, M.; Smirnova, I. Reactive Separations for In Situ Product Removal of Enzymatic Reactions: A Review. *Chem. Ing. Tech.* **2019**, *91*, 1522–1543. [CrossRef]
50. Manthiram, A.; Zhao, X.; Li, W. Developments in membranes, catalysts and membrane electrode assemblies for direct methanol fuel cells (DMFCs). *Funct. Mater. Sustain. Energy Appl.* **2012**, 312–369. [CrossRef]
51. Su, Y.; Lv, H.; Zhou, W.; Zhang, C. Review of the Hydrogen Permeability of the Liner Material of Type IV On-Board Hydrogen Storage Tank. *World Electr. Veh. J.* **2021**, *12*, 130. [CrossRef]

52. Kian, K.; Woodall, C.M.; Wilcox, J.; Liguori, S. Performance of Pd-Based Membranes and Effects of Various Gas Mixtures on H₂ Permeation. *Environments* **2018**, *5*, 128. [CrossRef]
53. Paglieri, S.N.; Way, J.D. Innovations in palladium membrane research. *Sep. Purif. Methods* **2002**, *31*, 1–169. [CrossRef]
54. Pinacci, P.; Basile, A. *Palladium-Based Composite Membranes for Hydrogen Separation in Membrane Reactors*; Elsevier: Amsterdam, The Netherlands, 2013; pp. 149–182.
55. Allevi, C.; Collodi, G. Hydrogen production in IGCC systems. In *Integrated Gasification Combined Cycle (IGCC) Technologies*; Elsevier: Amsterdam, The Netherlands, 2017; pp. 419–443.
56. Elkina, I.B.; Meldon, J.H. Hydrogen transport in palladium membranes. *Desalination* **2002**, *147*, 445–448. [CrossRef]
57. Yun, S.; Oyama, S.T. Correlations in palladium membranes for hydrogen separation: A review. *J. Membr. Sci.* **2011**, *375*, 28–45. [CrossRef]
58. Shu, J.; Grandjean, B.P.A.; Van Neste, A.; Kaliaguine, S. Catalytic palladium-based membrane reactors: A review. *Can. J. Chem. Eng.* **1991**, *69*, 1036–1060. [CrossRef]
59. Turnbull, A. Hydrogen diffusion and trapping in metals. *Gaseous Hydrog. Embrittlement Mater. Energy Technol.* **2012**, 89–128. [CrossRef]
60. Flynn, G.; Yalkowsky, S.; Roseman, T. Mass transport Phenomena and Models: Theoretical Concepts. *J. Pharm. Sci.* **1974**, *63*, 479–510. [CrossRef] [PubMed]
61. Chen, W.-H.; Hsia, M.-H.; Chi, Y.-H.; Lin, Y.-L.; Yang, C.-C. Polarization phenomena of hydrogen-rich gas in high-permeance Pd and Pd–Cu membrane tubes. *Appl. Energy* **2014**, *113*, 41–50. [CrossRef]
62. Abdollahi, M.; Yu, J.; Liu, P.K.; Ciora, R.; Sahimi, M.; Tsotsis, T.T. Ultra-pure hydrogen production from reformat mixtures using a palladium membrane reactor system. *J. Membr. Sci.* **2012**, *390–391*, 32–42. [CrossRef]
63. McLeod, L.; Degertekin, F.; Fedorov, A. Determination of the rate-limiting mechanism for permeation of hydrogen through microfabricated palladium–silver alloy membranes. *J. Membr. Sci.* **2009**, *341*, 225–232. [CrossRef]
64. Holleck, G.L. Diffusion and solubility of hydrogen in palladium and palladium–silver alloys. *J. Phys. Chem.* **1970**, *74*, 503–511. [CrossRef]
65. Smirnov, L.I.; Gol'Tsov, V.A. Nonlinear and crossover effects in the diffusion penetration of hydrogen through a metallic membrane. *J. Eng. Phys. Thermophys.* **1988**, *55*, 981–985. [CrossRef]
66. Hurlbert, R.C.; Konecny, J.O. Diffusion of Hydrogen through Palladium. *J. Chem. Phys.* **1961**, *34*, 655–658. [CrossRef]
67. Katsuta, H.; Farraro, R.J.; McLellan, R.B. The diffusivity of Hydrogen in palladium. *Acta Metallurgica* **1979**, *27*, 1111–1114, ISSN 0001-6160. [CrossRef]
68. Caravella, A.; Barbieri, G.; Drioli, E. Concentration polarization analysis in self-supported Pd-based membranes. *Sep. Purif. Technol.* **2009**, *66*, 613–624. [CrossRef]
69. Roa, F.; Block, M.J.; Way, J. The influence of alloy composition on the H₂ flux of composite Pd–Cu membranes. *Desalination* **2002**, *147*, 411–416. [CrossRef]
70. Fuerst, T.F.; Humrickhouse, P.W.; Taylor, C.N.; Shimada, M. Surface effects on deuterium permeation through vanadium membranes. *J. Membr. Sci.* **2021**, *620*, 118949. [CrossRef]
71. Ali, J.K.; Newson, E.; Rippin, D. Deactivation and regeneration of Pd–Ag membranes for dehydrogenation reactions. *J. Membr. Sci.* **1994**, *89*, 171–184. [CrossRef]
72. Yamakawa, K.; Ege, M.; Ludescher, B.; Hirscher, M. Surface adsorbed atoms suppressing hydrogen permeation of Pd membranes. *J. Alloy. Compd.* **2003**, *352*, 57–59. [CrossRef]
73. Suzuki, A.; Yukawa, H. A Review for Consistent Analysis of Hydrogen Permeability through Dense Metallic Membranes. *Membranes* **2020**, *10*, 120. [CrossRef] [PubMed]
74. Caravella, A.; Barbieri, G.; Drioli, E. Modelling and simulation of hydrogen permeation through supported Pd-alloy membranes with a multicomponent approach. *Chem. Eng. Sci.* **2008**, *63*, 2149–2160. [CrossRef]

Article

Study on the Influence of Geometric Characteristics of Grain Membranes on Permeability Properties in Porous Sandstone

Run Shi ¹, Huaiguang Xiao ^{2,*}, Chengmeng Shao ³, Mingzheng Huang ⁴ and Lei He ²

¹ Nick Ceiling Pty. Ltd., St Peters, NSW 2044, Australia; aushirun@gmail.com

² School of Civil Engineering, Southeast University, Nanjing 211189, China; helei_civil@seu.edu.cn

³ The 3rd Construction Company Ltd. of China 16th Corporation, Huzhou 313000, China; shaochengmeng.16g@crcc.cn

⁴ Chang'an-Dublin International College of Transportation, Chang'an University, Xi'an 710018, China; mingzheng.huang@ucdconnect.ie

* Correspondence: huaiguangxiao@seu.edu.cn

Abstract: Studying the influence of grain characteristics on fluid flow in complex porous rock is one of the most important premises to reveal the permeability mechanism. Previous studies have mainly investigated the fluid flow laws in complex rock structures using an uncontrollable one single parameter of natural rock models or oversimplified control group models. In order to solve these problems, this paper proposes a novel method to reconstruct models that can independently control one single parameter of rock grain membranes based on mapping and reverse-mapping ideas. The lattice Boltzmann method is used to analyze the influence of grain parameters (grain radius, space, roundness, orientation, and model resolution) on the permeability characteristics (porosity, connectivity, permeability, flow path, and flow velocity). Results show that the grain radius and space have highly positive and negative correlations with permeability properties. The effect of grain roundness and resolution on permeability properties shows a strong regularity, while grain orientation on permeability properties shows strong randomness. This study is of great significance to reveal the fluid flow laws of natural rock structures.

Keywords: porous sandstone; grain membranes; mapping method; lattice Boltzmann; permeability

1. Introduction

Rock is a kind of complex geological body containing a large number of continuous and discontinuous structures. These discontinuous structures cause the penetrability of the rock at any scale, and they dominate the hydrological behavior of the rock. Therefore, the study of fluid flow laws in discontinuous structures has great significance for the prevention and control of inrush water in rock mass engineering [1] and the improvement of oil extraction [2] and gas extraction [3,4] efficiency. The discontinuous structures of the rock are extremely complex, so the structures should be quantitatively characterized, and then the fluid flow laws in the rock are possible to be revealed by analyzing the fluid behavior with different characterization parameters.

In order to characterize the discontinuous structures of the rock and obtain the fluid flow behaviors in the structures, a variety of research methods have been adopted. For the permeability experiments of the rock in the laboratory, computerized tomography (CT) can capture the discontinuous structure inside the rock [5], and the steady-state and non-steady-state methods can measure the rock permeability [6–8], and nuclear magnetic resonance (NMR) can capture the fluid flow process to some extent [9]. The pore structure model and permeability obtained by these methods are realistic. However, the fluid flow paths in rock structures are challenging to catch with real-time and high fidelity. Furthermore, due to the random structure of natural rock, the quantitative characterization parameters between different rocks do not have regularity, so the permeability laws of

rock structure are hard to study. To reveal the fluid flow paths, the theoretical analysis method for rock permeability can realize quantitative characterization parameters between different rock models with a single variable [10]. It can also obtain permeability results and visual flow paths that can be used to analyze the influence of rock structural parameters on permeability behavior. However, this method can only solve the permeability behaviors of simplified models and cannot solve the nonlinear permeability problem of complex rock structures. With the rapid development of high-performance computing platforms and numerical algorithms, the numerical simulation method has been widely used in permeability analysis of complex structures in recent years. This method has the advantages of solving complex problems, strong visualization, and low cost.

Constructing a numerical model that can simulate the natural rock structures (real control group) and control the independent change of characterization parameters (single control variable) is vital to study the fluid flow laws in complex rock structures based on the numerical simulation method. The modeling of pore structures is usually divided into direct and indirect methods. The direct methods refer to obtain two-dimensional or three-dimensional natural rock pore structures using physical equipment (such as the camera, CT) and image processing technology [11]. The model established by this method can reproduce the structural characteristics of the natural rock (real control group), and the permeability behavior of the natural rock can be obtained with the support of scientific CFD algorithms. However, due to the random differences between different rocks, the characterization parameters are intermingled with each other, which causes the hard to realize independent variations of the characterization parameters. The indirect method refers to using random distribution to reproduce some parameter characterizations in a new model. Parameterization methods mainly include the fractal method [12], the Gaussian field method [13], the simulated annealing method [14], the QSGS parameter method [15], and the Markov chain Monte Carlo method [16]. These methods can establish plausible pore models and control the single variation of characteristic parameters, but the complementary phase (grain structure) of pore structures is difficult to reflect the morphology of natural grains, which cannot form a real control group. Xiao et al. [17,18] used digital twinning technology and texture synthesis method to build highly realistic rock meso-structures to keep the pore and grain structures natural and realistic. However, these methods cannot achieve single and independent changes in characterization parameters.

Due to the high complexity and randomness of pore structures, it is challenging to describe the pore structures accurately. The boundary (membranes) of mineral grains delineates the pore structures over time by geological processes. In other words, the pore structures that are structurally complementary to the grains are the product of the interaction between mineral grains. Therefore, if the grain structures of the rock can be accurately described, the pore structures will also be accurately described. Compared with the complex pore structures, the relatively regular grain structures can reveal the fluid flow laws of porous rock more easily. Many scholars have studied the permeability behaviors by changing the space [19], radius [10], and roundness [20] of grains and obtained helpful conclusions. However, the control groups in this research were simplified rock models, and they could not accurately reflect the actual permeability behaviors. In this case, the models with various parameters derived from these simplified control groups are likely to reflect non-accurate permeability laws. Although the above studies can control the single variable of the representational parameters, the results of the control groups are not convincing.

With regard to permeability simulation, the finite volume method, finite difference method, and finite element method, based on the Navier–Stokes (NS) equations, are mainstream algorithms in most commercial software. However, the NS-based methods for solving the fluid flow problems in complex porous media are challenging because the mesh of these methods is difficult to guarantee both model and computational reliability. By contrast, the lattice Boltzmann method (LBM) is based on the pixel (lattice) scale, which

can reproduce complex pore structures and give accurate computational fluid results. The advantages of LBM in complex porous media have been applied in many studies, such as heat transfer [21,22] and water seepage [17].

This paper aims to study the influence of geometry characteristics of grains on fluid flow laws by changing the geometric parameters of grains in natural rocks based on natural rocks as the control group and the controlling single variable method. The two-dimensional image of the natural pore sandstone provides an actual control group, and the discrete mapping and reverse-mapping ideas are used to achieve single and controllable grain parameters. Furthermore, the lattice Boltzmann method is used to reveal the fluid flow laws of the pore sandstone model under different characterization parameters.

2. Materials and Methods

2.1. Materials

The model in this research is from Oklahoma's Permian-age Sandstone [23]. As shown in Figure 1a, the physical size of the porous sandstone is approximate to $1\text{ mm} \times 1\text{ mm}$, in which the mineral grains are off-white with a diameter of about 0.2 mm , and the pores are dyed blue. In order to study the influence of mineral grains in this porous sandstone on permeability behavior, the manual delineate method was used to separate the 71 grains completely, as shown in Figure 1b. Then, image processing technology was used to identify the mineral grain boundary and obtain the skeleton structure of the boundary, as shown in Figure 1c. The area, equivalent radius, perimeter, and roundness of separated mineral grains are shown in Table 1.

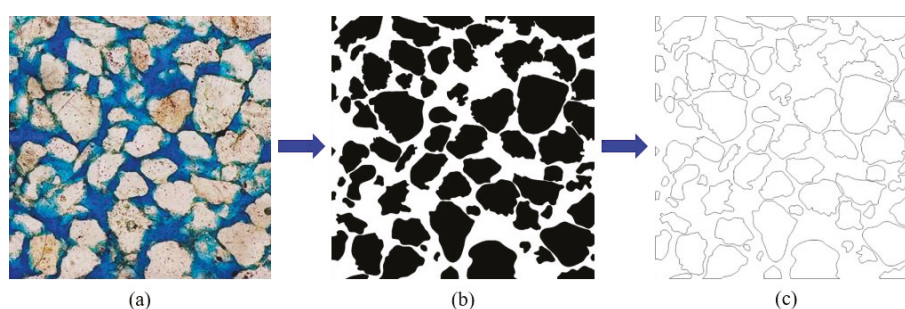


Figure 1. The process for obtaining grain boundaries (membranes) of porous sandstone. (a) Porous sandstone; (b) Grain separation; (c) Grain boundaries.

Table 1. Grain geometry parameters (sorted by area from large to small).

No.	Area /Pixel	Equivalent Radius /Pixel	Perimeter /Pixel	Roundness	No.	Area /Pixel	Equivalent Radius /Pixel	Perimeter /Pixel	Roundness
1	16,089	71.56	499.92	0.77	37	3246	32.15	219.75	0.76
2	13,745	66.14	476.77	0.70	38	3219	32.01	252.89	0.59
3	11,868	61.46	446.09	0.69	39	2664	29.12	245.94	0.55
4	11,452	60.38	422.87	0.75	40	2573	28.62	210.94	0.67
5	11,266	59.88	428.02	0.72	41	2418	27.74	193.40	0.74
6	10,784	58.59	621.10	0.35	42	2312	27.13	235.47	0.49
7	9309	54.44	396.04	0.71	43	2064	25.63	234.90	0.45
8	9080	53.76	430.48	0.59	44	2009	25.29	188.76	0.66
9	7983	50.41	484.83	0.41	45	1842	24.21	230.67	0.40
10	7930	50.24	370.31	0.72	46	1837	24.18	160.17	0.83
11	7320	48.27	343.00	0.72	47	1734	23.49	168.89	0.70
12	7146	47.69	339.35	0.73	48	1710	23.33	166.04	0.73
13	6693	46.16	373.26	0.55	49	1681	23.13	208.37	0.45
14	6637	45.96	400.66	0.49	50	1545	22.18	176.45	0.57
15	6498	45.48	332.51	0.68	51	1354	20.76	148.44	0.72
16	6397	45.13	362.81	0.57	52	1188	19.44	133.53	0.78

Table 1. Cont.

No.	Area /Pixel	Equivalent Radius /Pixel	Perimeter /Pixel	Roundness	No.	Area /Pixel	Equivalent Radius /Pixel	Perimeter /Pixel	Roundness
17	6204	44.44	317.68	0.70	53	975	17.62	114.47	0.85
18	6035	43.83	331.56	0.67	54	964	17.52	132.79	0.69
19	5975	43.61	338.20	0.62	55	949	17.38	136.12	0.59
20	5961	43.56	334.25	0.63	56	891	16.84	129.42	0.63
21	5671	42.49	296.29	0.74	57	816	16.12	107.51	0.80
22	5175	40.58	348.43	0.50	58	740	15.35	102.46	0.80
23	5079	40.21	349.42	0.49	59	682	14.73	144.48	0.38
24	5060	40.13	281.61	0.74	60	626	14.12	98.63	0.78
25	5013	39.94	288.02	0.69	61	563	13.39	120.57	0.47
26	4881	39.42	277.90	0.74	62	526	12.94	124.82	0.39
27	4497	37.83	267.34	0.73	63	521	12.88	89.63	0.74
28	4242	36.75	266.25	0.70	64	521	12.87	89.75	0.74
29	4216	36.63	288.08	0.61	65	498	12.59	104.58	0.53
30	4127	36.24	279.46	0.62	66	406	11.37	72.70	0.88
31	4054	35.92	278.28	0.62	67	268	9.24	64.43	0.76
32	3944	35.43	265.95	0.63	68	252	8.95	63.38	0.74
33	3885	35.16	291.08	0.52	69	243	8.80	54.94	0.91
34	3647	34.07	252.40	0.72	70	156	7.06	56.72	0.63
35	3506	33.41	231.89	0.74	71	144	6.76	46.05	0.79
36	3295	32.38	303.86	0.43					

2.2. Mapping and Reverse-Mapping Method

Each grain in the porous sandstone is considered intact and homogeneous, and each grain model can be abstracted as a topologically closed set (as shown in Figure 2), which is a two-dimensional infinite point set in Euclidean space. There is much redundancy in describing topologically closed sets using two-dimensional coordinates in Euclidean space. Combined with the dimensionality reduction idea of manifolds, topologically closed sets can be accurately described using boundaries, as shown in Figure 2. In other words, if the grain boundary is accurately described, the intact grain will also be accurately described. The grain boundary in natural rocks is characterized by high complexity and randomness, so it is not easy to characterize the grain boundary with geometric parameters accurately. Substitutively, the discrete and high-density points is an effective method to describe complex boundary structure.

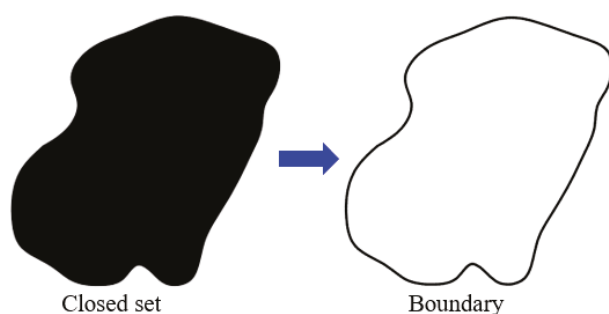


Figure 2. Dimension reduction of grain topologically closed sets.

In order to study the geometric characteristics of the grains (such as size, position, roundness, and orientation), parameterized analysis of the grain characteristics is required. The radius of an equivalent circle, the centroid, the distance between grain boundary and the equivalent circle, the angle between the long axis and horizontal line represent the size, the position, the roundness, and orientation, respectively. To describe the irregular boundary of the grain, discrete points of the boundary are mapped onto the circle. All

discrete points on the boundary can be recorded only by recording two sets of parameters (slope of the centroid and boundary point, mapping distance between the circle and boundary) under the condition of constant centroid and radius, as shown in Figure 3a. Thus, an unique boundary point can be determined by given an endpoint of a line segment (centroid), a slope, and a signed distance (radius and mapping distance). The original model can be perfectly reserve-mapping with two sets of parameters (slope and mapping distance). As shown in Figure 3b, the radius, centroid position, mapping distance, and slope can be adjusted in the reserve-mapping process to change the size, spacing, roundness, and orientation parameters of grains, respectively, by using Formulas (1)–(4)

$$k_i = \tan \alpha_i = \frac{y_{i,j} - a_i}{x_{i,j} - b_i} \quad (1)$$

$$d_i = \pm \sqrt{(y_{i,j} - a_i)^2 + (x_{i,j} - b_i)^2} - r_i \quad (2)$$

$$x_{i,j} = a_i + \text{sign}(a_i - x_{i,j}) \times \frac{r_i + d_i}{\sqrt{\tan^2 \alpha_i + 1}} \quad (3)$$

$$y_{i,j} = b_i + \text{sign}(a_i - x_{i,j}) \times \tan^2 \alpha \times \frac{r_i + d_i}{\sqrt{\tan^2 \alpha_i + 1}} \quad (4)$$

(a_i, b_i) —grain centroid position; r_i —grain equivalent radius; d_i —grain mapping distance; α_i —grain orientation; $(x_{i,j}, y_{i,j})$ —the j -th point on the boundary of the i -th grain.

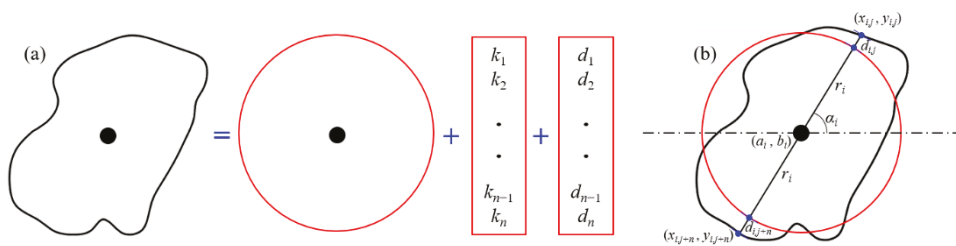


Figure 3. The mapping and reserve-mapping principle. (a) The mapping and reserve-mapping process between irregular boundary and circle boundary; (b) Parameters relationships between irregular boundary and circle boundary.

2.2.1. Size

Under the condition that the grain centroid coordinates, mapping distance, and slope remain unchanged, a single variation in grain size can be achieved by adjusting the radius, as shown in Figure 4. Assume that the grain radius increases by Δr_i , then the grain radius after the change is

$$r'_i = r_i + \Delta r_i \quad (5)$$

The results of grain size change is shown in Figure 5.

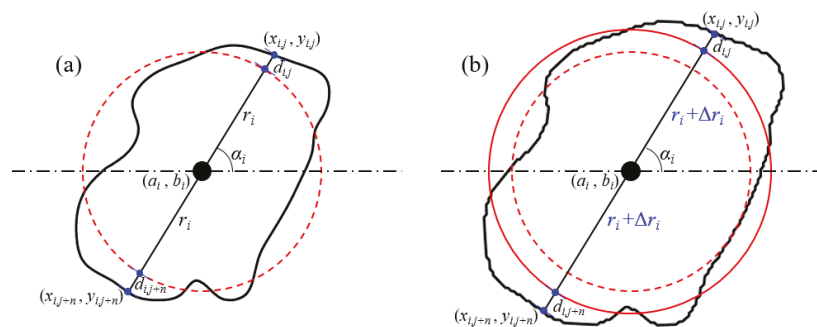


Figure 4. The principle of grain size change. (a) Original relationship between grain boundary and mapping circle. (b) The relationship between them with the grain radius increasing Δr_i .

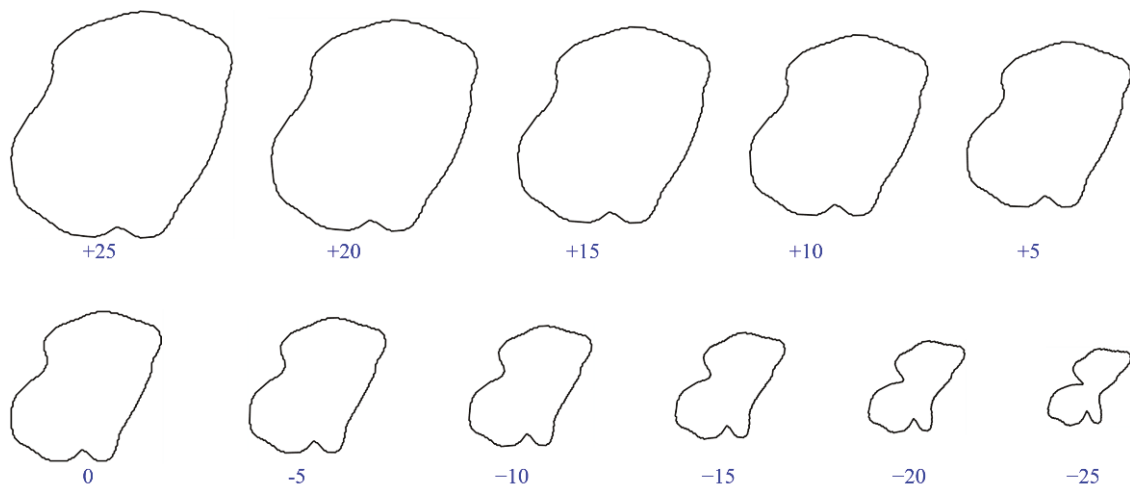


Figure 5. The results of grain size change.

2.2.2. Position

Under the condition that grain radius, mapping distance, and slope remain unchanged, the only change of grain position and spacing can be realized by adjusting centroid position, as shown in Figure 6. Assume that Δa_i and Δb_i are added in the horizontal and vertical coordinates of the grain centroid, respectively, then the changed grain position is

$$(a'_i, b'_i) = (a_i + \Delta a_i, b_i + \Delta b_i) \quad (6)$$

The results after the change of grain position is shown in Figure 7.

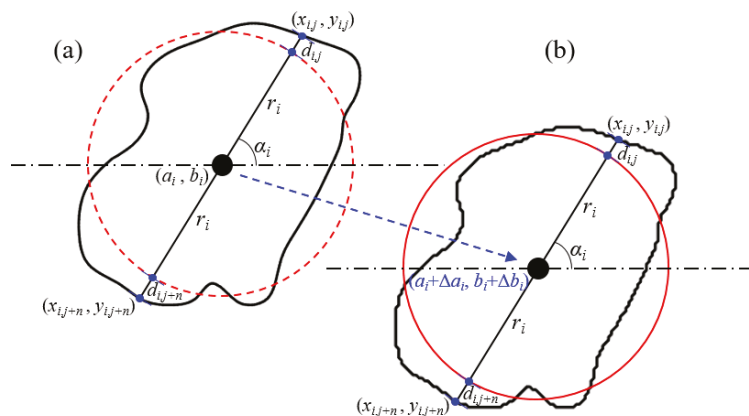


Figure 6. The principle of grain position change. (a) Original relationship between grain boundary and mapping circle. (b) The relationship between them with the coordinates increasing Δa_i and Δb_i .

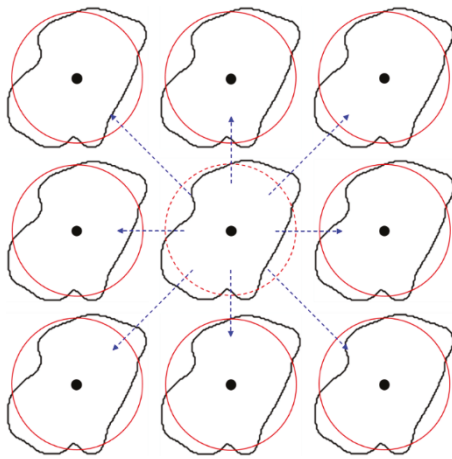


Figure 7. The results of the grain position change.

2.2.3. Roundness

Under the condition that the centroid coordinates, radius, and slope of the grain remain unchanged, a single change in the roundness of the grain can be achieved by adjusting the mapping distance, as shown in Figure 8. Assuming that the mapping distance increases Δd_{ij} , then the mapping distance after the change is

$$d'_{ij} = d_{ij} + \Delta d_{ij} \quad (7)$$

The result after changing the mapping distance of grains is shown in Figure 9.

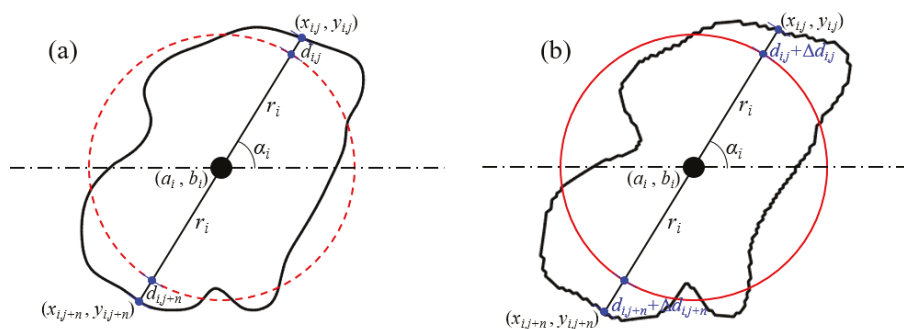


Figure 8. The principle of grain roundness change. (a) Original relationship between grain boundary and mapping circle. (b) The relationship between them with the mapping distance increasing Δd_{ij} .

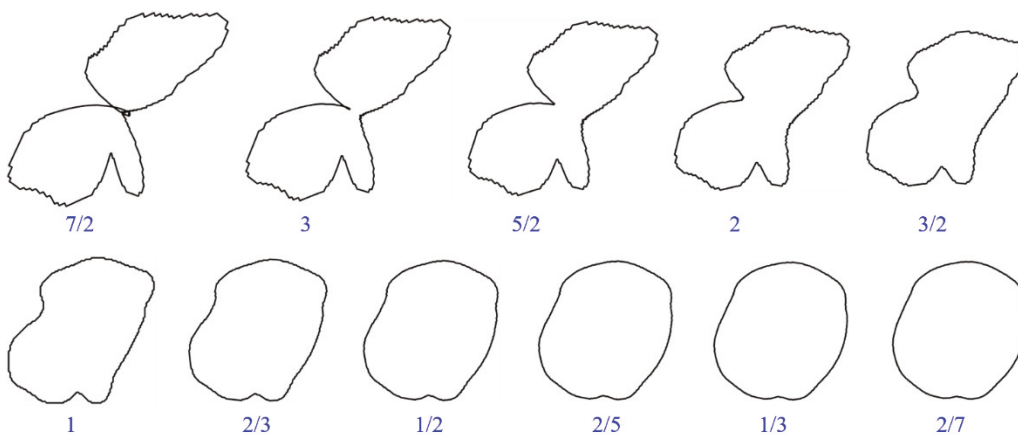


Figure 9. The results of grain roundness change.

2.2.4. Orientation

Under the condition that the centroid coordinates, radius, and mapping distance of grains remain unchanged, the single control variable grain orientation can be achieved by adjusting the slope of grains, as shown in Figure 10. Suppose the grain orientation rotates $\Delta\alpha_i$ counterclockwise, then the slope of the point on the grain boundary after rotation is

$$k'_i = \tan(\alpha_i + \Delta\alpha_i) = \frac{\tan\alpha_i + \tan\Delta\alpha_i}{1 - \tan\alpha_i \tan\Delta\alpha_i} = \frac{k_i + \tan\Delta\alpha_i}{1 - k_i \tan\Delta\alpha_i} \quad (8)$$

The results of grain orientation changes are shown in Figure 11.

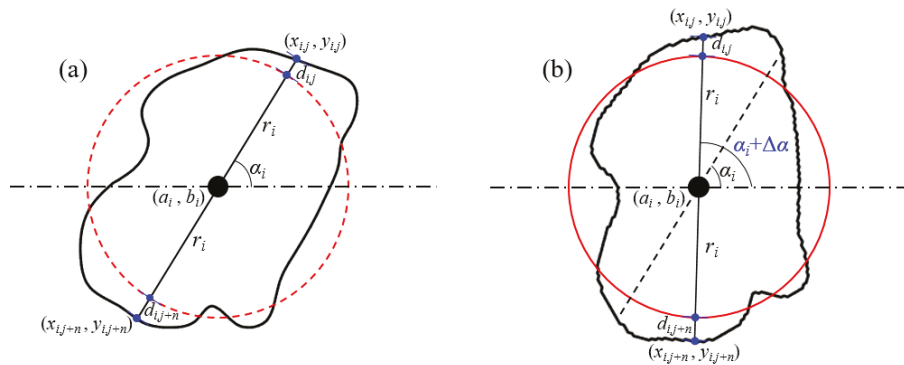


Figure 10. The principle of grain orientation change. (a) Original relationship between grain boundary and mapping circle. (b) The relationship between them under a $\Delta\alpha_i$ counterclockwise rotation.

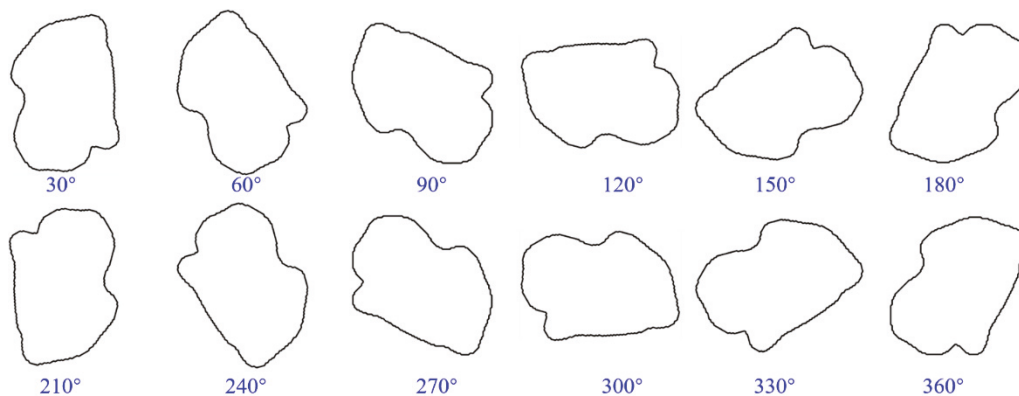


Figure 11. The results of grain orientation change.

2.3. Lattice Boltzmann Method

The lattice Boltzmann method is a computational fluid dynamics method based on the kinetic theory. Compared with other CFD methods, it is good at solving the fluid flow process in complex structures. In this paper, the classical BGK solution model is adopted, and the collision and streaming rules between grains are used to calculate fluid seepage rules. The evolution equation as follows

$$f(x + e\delta t, e, t + \delta t) - f(x, e, t) = -\frac{1}{\tau} [f(x, e, t) - f^{eq}(x, e, t)] \quad (9)$$

where f is a function of variables t, x, e , and $f(t, x, e)$ represents the density distribution of grains which velocities are ζ at the position x at time t ; τ refers to the average time interval between two collisions, also known as slack time or relaxation time; is the equilibrium distribution function.

In order to solve the Boltzmann–BGK (Bhatnagar–Gross–Krook) equation by discretizing the evolution equation, the Taylor expansion equation of Maxwell’s equilibrium state distribution function is

$$f_i^{eq} = w_i \rho \left[1 + \frac{3(e_i \cdot u)}{c^2} + \frac{9(e_i \cdot u)^2}{2c^4} - \frac{3u^2}{2c^2} \right] \quad (10)$$

where w_i is the weight coefficient; ρ is the density; e_i is the discrete velocity; u is the velocity, and c is the lattice velocity.

In this research, the phase space discrete model of D2Q9 is adopted, as shown in Figure 12. According to the D2Q9 model, the discrete velocity set and weight coefficient of $\mathbf{e}$ are respectively calculated as follows:

$$e_i = c \begin{pmatrix} 0 & 1 & 0 & -1 & 0 & 1 & -1 & -1 & 1 \\ 0 & 0 & 0 & 0 & -1 & 1 & 1 & -1 & -1 \end{pmatrix} \quad (11)$$

$$w_i = \begin{cases} 4/9, & e_i^2 = 0 \\ 1/9, & e_i^2 = c^2 \\ 1/36, & e_i^2 = 2c^2 \end{cases} \quad (12)$$

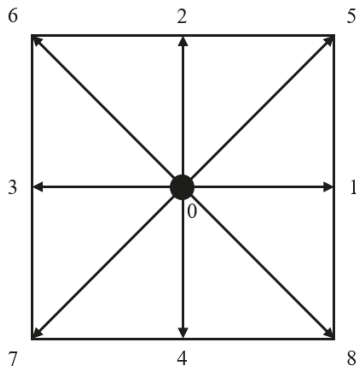


Figure 12. D2Q9 model.

Based on the Chapman–Enskog expansion formula, the macroscopic fluid density ρ , velocity $\mathbf{u}$, pressure p , and viscosity coefficient ν can be derived through the following equations:

$$\rho = \sum_i f_i \quad (13)$$

$$\mathbf{u} = \sum_i f_i e_i / \rho \quad (14)$$

$$p = c_s^2 \rho \quad (15)$$

$$\nu = \frac{c^2}{3} (\tau - 0.5) \delta \quad (16)$$

The standard rebound boundary is adopted in this research. The boundary of the model is left in and right out, and the other boundaries are closed.

3. Results

In this section, the above methods are used to reconstruct the models of porous sandstone, and the permeability laws affected by the parameters of grain membranes are analyzed based on the reconstructed models. The simulation parameters in this paper are derived from the literature [17], which has been verified by the physical experiments.

3.1. Grain Radius

Grain radius determines grain sizes, which affects the structure and connectivity of the pores surrounded by the grain membrane. In order to study the influence of membrane structure radius on pore structure characteristics, the equivalent grain radius in the original image (red box line) is reduced (-10 , -8 , -6 , -4 , and -2 pixels) and increased (2 and 4 pixels) under the condition that the model size (700×700 pixels) remain constant, as shown in Figure 13a. When the equivalent grain radius is small, the pore channels formed by grain membranes have large sizes and good connectivity. With the increase of the equivalent grain radius, the distance between grains gradually reduces, and then contact or overlap, making the channels formed by the grain membranes become narrow, and the connectivity decreases gradually.

In order to study the effect of the pore structure changed by the equivalent grain radius on the permeability characteristics, the permeability, and flow path under different grain radii were analyzed, respectively. As shown in Figure 13b, with the increase of equivalent grain radius, permeability presents a decrease in an approximate power function type. The permeability of the original model was 2228 mD. When the equivalent grain radius was reduced by 10 pixels, the permeability of the model was 36,636 mD, which is exceptionally high. When the equivalent grain radius was increased by 5 pixels, the permeability of the model was 15 mD, which is extremely low. As shown in Figure 13c, when the equivalent grain radius was small, the number of fluid flow channels from left to right is large, and the flow velocity was high. With the increase of the equivalent grain radius, both the number of channels and flow velocity decrease gradually. When the equivalent grain radius was increased by 4 pixels, only one narrow flow channel and the flow velocity was very low.

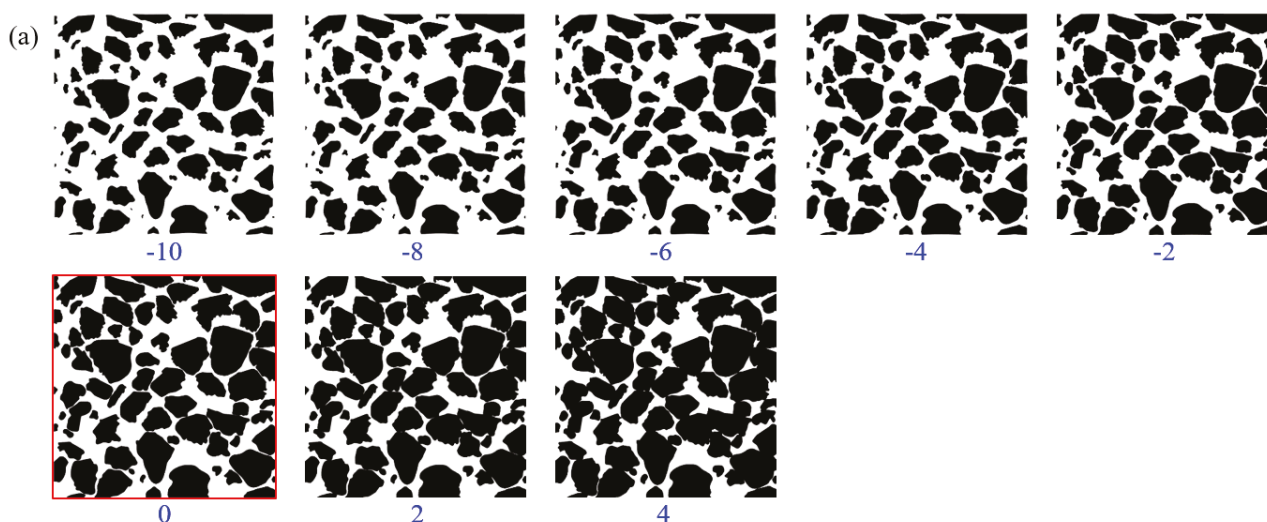


Figure 13. *Cont.*

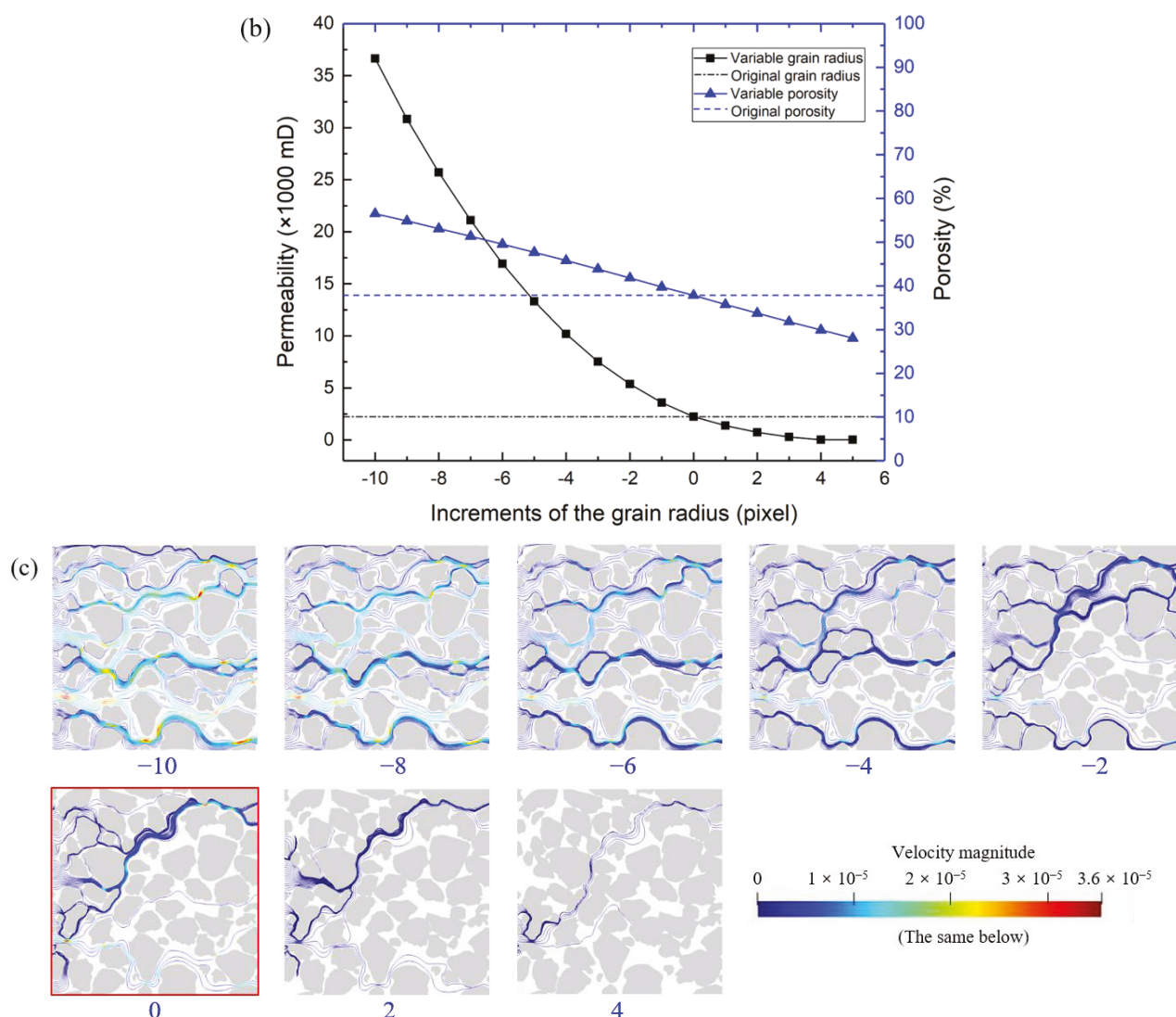


Figure 13. Influence of grain radius on permeability. (a) Pore models with different grain radiuses; (b) porosity and permeability of pore models with different grain radiuses; (c) flow paths and velocity of pore models with different grain radiuses.

3.2. Grain Space

In porous sandstones, pore media is usually filled between mineral grains, so the larger the space between the grains, the greater the pore media will be. Under the condition that the size and shape of the grains are constant, increasing grain space, the model size and spacing are raised by the same multiple. The length of the original image (red box line) is 700 pixels while adjusting the space by 1/1.08, 1/1.04, 1.04, 1.08, 1.12, 1.16, and 1.20 times and the corresponding model lengths are 648, 673, 728, 756, 784, 812, and 840 pixels, respectively. As shown in Figure 14a, when the grain space of the original model is reduced, the grains contact and overlap, which have similar characteristics to that of increasing the grain radius. With the increasing grain space, the pore channels between grains become wide, and the connectivity becomes well.

As shown in Figure 14b, the permeability of the original model is 2228 mD. When the grain space reduces, the permeability gradually decreases until it reaches zero. The permeability increases linearly with the rise of grain space. When the spacing is increased by 1.2 times, the permeability reaches 27,723 mD. As shown in Figure 14c, the flow channel and velocity are tiny when the spacing is minimal. With increasing grain spacing, the flow channel and velocity increase.

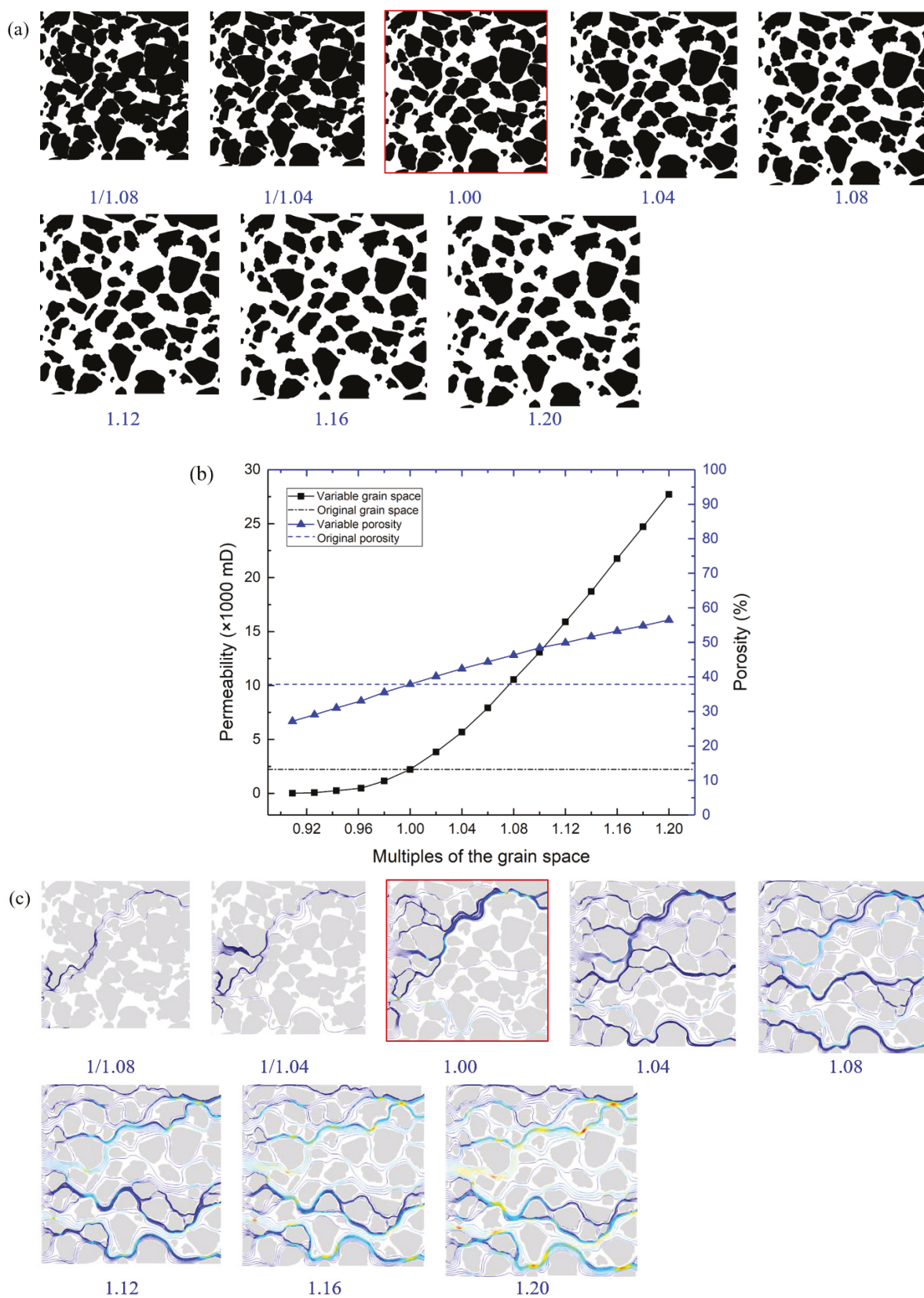


Figure 14. Influence of grain space on permeability. (a) Pore models with different grain spaces; (b) porosity and permeability of pore models with different grain spaces; (c) flow paths and velocity of pore models with different grain spaces.

3.3. Grain Roundness

Mineral grains of natural rocks are irregular, and their irregularity largely determines the shape of the membrane between solid and liquid, thus affecting the permeability characteristics. The grain roundness of the original model (red box line) is extremely diverse, ranging from approximate round grain shapes to very complex shapes. In order to study the influence of grain roundness on permeability characteristics, all grains in the rock model are reduced or increased by changing the mapping distance on the equivalent circle under the condition that the model size remains unchanged, as shown in Figure 15a. When the roundness is tiny, the grain complexity is high with a long major-axis and a short minor-axis. The increase of the major axis will make the grains contact or overlap and reduce the connectivity of the pores. As the roundness of grains increases, the major-axis gradually decreases while the minor-axis gradually increases, and the shape of grains becomes more and more round. Thus, pore connectivity and porosity show a slow increase and then stabilize, as shown in Figure 15b.

When the grain roundness is small, the permeability is low, as shown in Figure 15b. With the increase of roundness, permeability increases rapidly at first and then decreases slowly. When the roundness is 1.8 times of the original model, the maximum permeability reaches 5022 mD. As shown in Figure 15c, the flow channel and velocity increased rapidly and then decreased slowly with the increase of roundness.

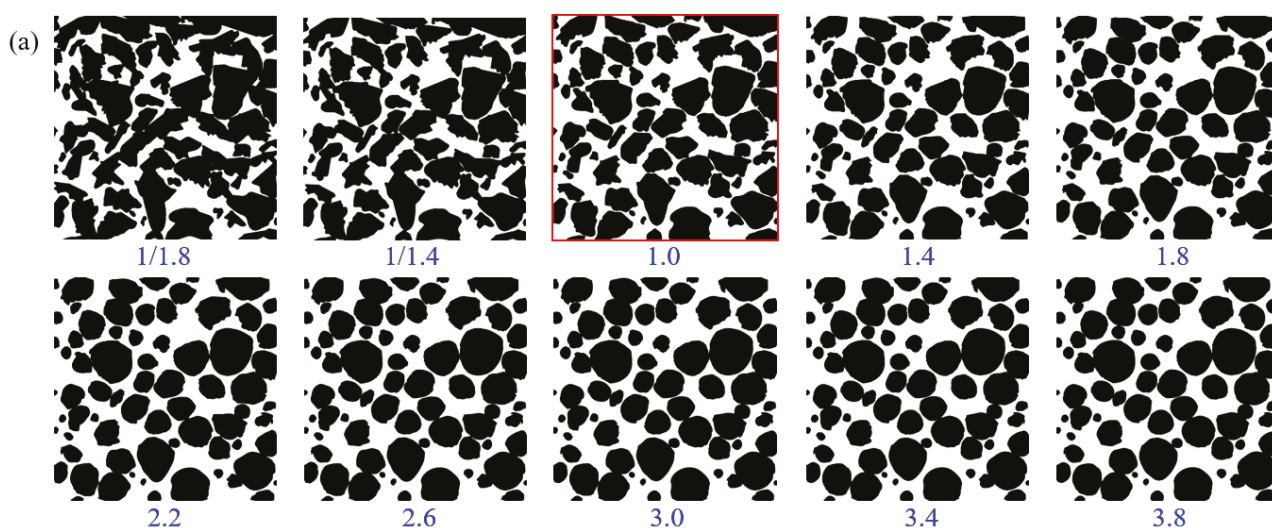


Figure 15. *Cont.*

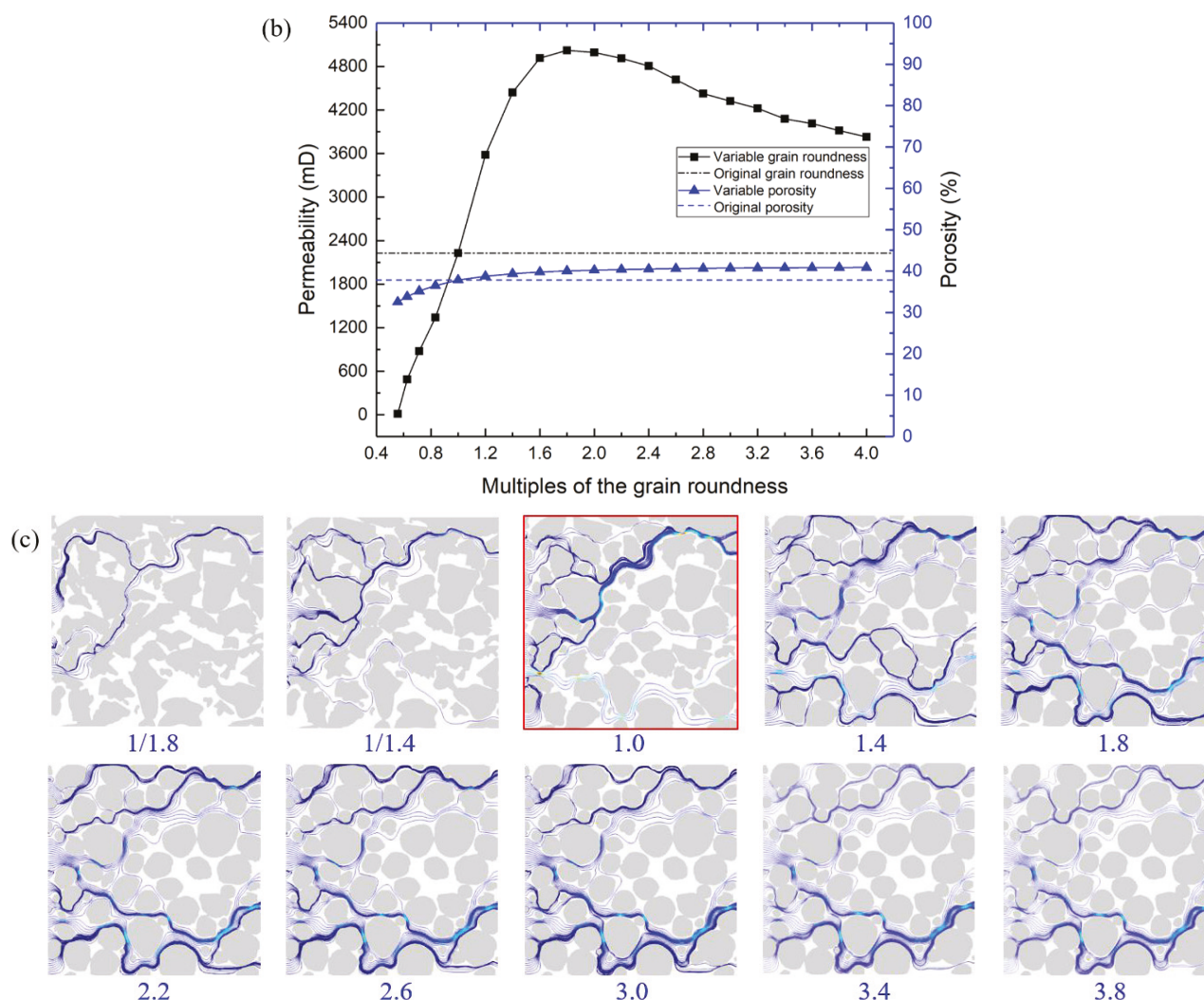


Figure 15. Influence of grain roundness on permeability. (a) Pore models with different grain roundness; (b) porosity and permeability of pore models with different grain roundness; (c) flow paths and velocity of pore models with different grain roundness.

3.4. Grain Orientation

Grains in natural rocks have diverse orientations, and grain orientation mainly affects the contact relationship between adjacent grains, including separation, tangency, or intersection. In order to reveal the influence of grain orientation on permeability characteristics, different orientated grain models are obtained by rotated counterclockwise at the same angle of all grains under the condition that the model size, grain size, and shape remained unchanged, as shown in Figure 16a. The change of grain orientation alters the pore structure and connectivity formed between adjacent grains and then affects the pore structure characteristics of the whole model. As shown in Figure 16b, the rotation angle of grain orientation has little influence on the porosity. The difference between the maximum and minimum porosity is only 5.75%. When the rotation angle of grain orientation is between 0–180°, the porosity presents a slow increase and then slowly decrease, and the porosity change law between 180° and 350° shows a similar tendency to that between 0° and 180°.

As shown in Figure 16b, with the change of grain orientation rotation angle (every 10°), there is no strong regularity between permeability and rotation angle. Only at an angle of 210°, was the model permeability (3139 mD) larger than the original permeability. The model permeability at some angles was almost zero (such as 20°, 30°, 40°, 60°,

70°, 260°, 290°, 300°, and 310°). At other angles, the permeability fluctuated randomly between 0 and 2228 mD (the permeability of the original model). The effect of grain orientation on permeability had strong randomness. As shown in Figure 16c, with the change of grain rotation angle, the flow channel and velocity have a large random change. The fluid in the model with very low permeability could not flow from the left to the right side of the model.

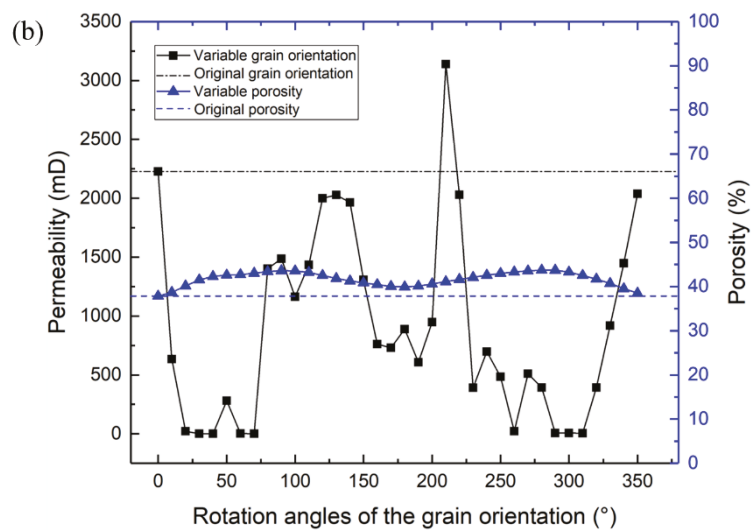
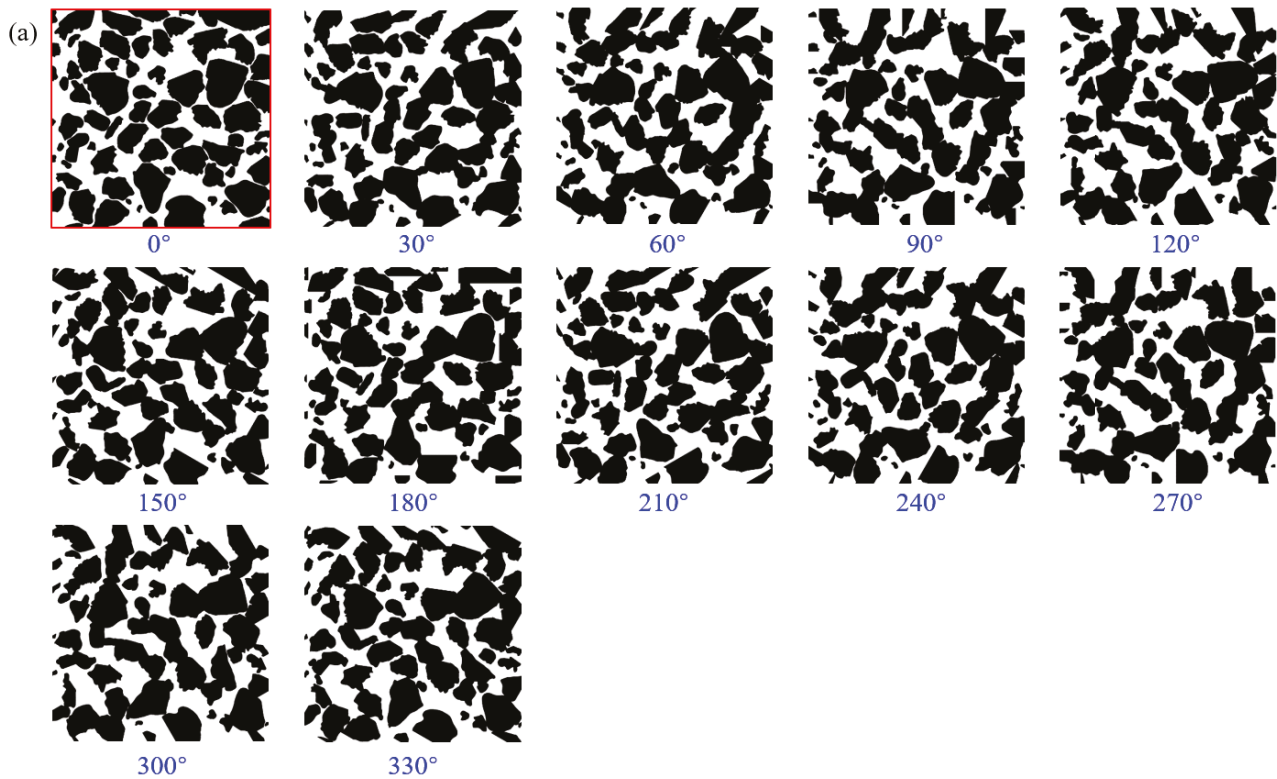


Figure 16. Cont.

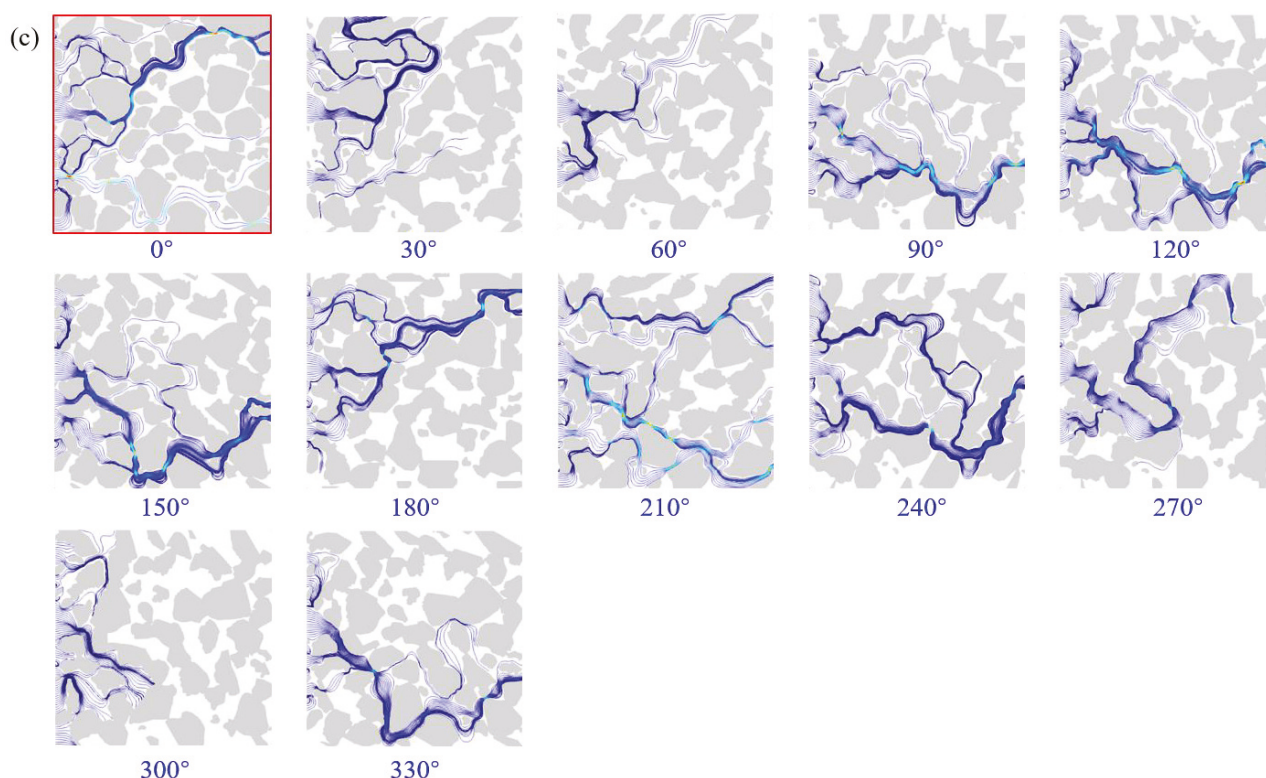


Figure 16. Influence of grain orientation on permeability. (a) Pore models with different grain orientations; (b) porosity and permeability of pore models with different grain orientations; (c) flow paths and velocity of pore models with different grain orientations.

3.5. Model Resolution

The lattice Boltzmann method, based on image pixel, was used to calculate the permeability of pore models. A pixel is a relative scale, which can represent different physical dimensions. To analyze the influence of image models under different resolutions on permeability characteristics, this study obtained models with the side length of 200, 250, 300, 350, 400, 450, 500, 550, 600, and 650 pixels, as shown in Figure 17a. The results show the pore structures between grains only change with the resolution, and its shape did not change, so the change of model resolution did not affect the porosity, as shown in Figure 17b.

With the increase of model resolution, the permeability gradually increased and then became stable, as shown in Figure 17b. When the model side length was 200 pixels, the minimum permeability was 1463 mD. When the model side length was 450 pixels, the permeability was 2193 mD, similar to the 2228 mD at 700 pixels. As shown in Figure 17c, the change of model resolution had little influence on the seepage path, but the seepage velocity gradually increases when the resolution is higher.

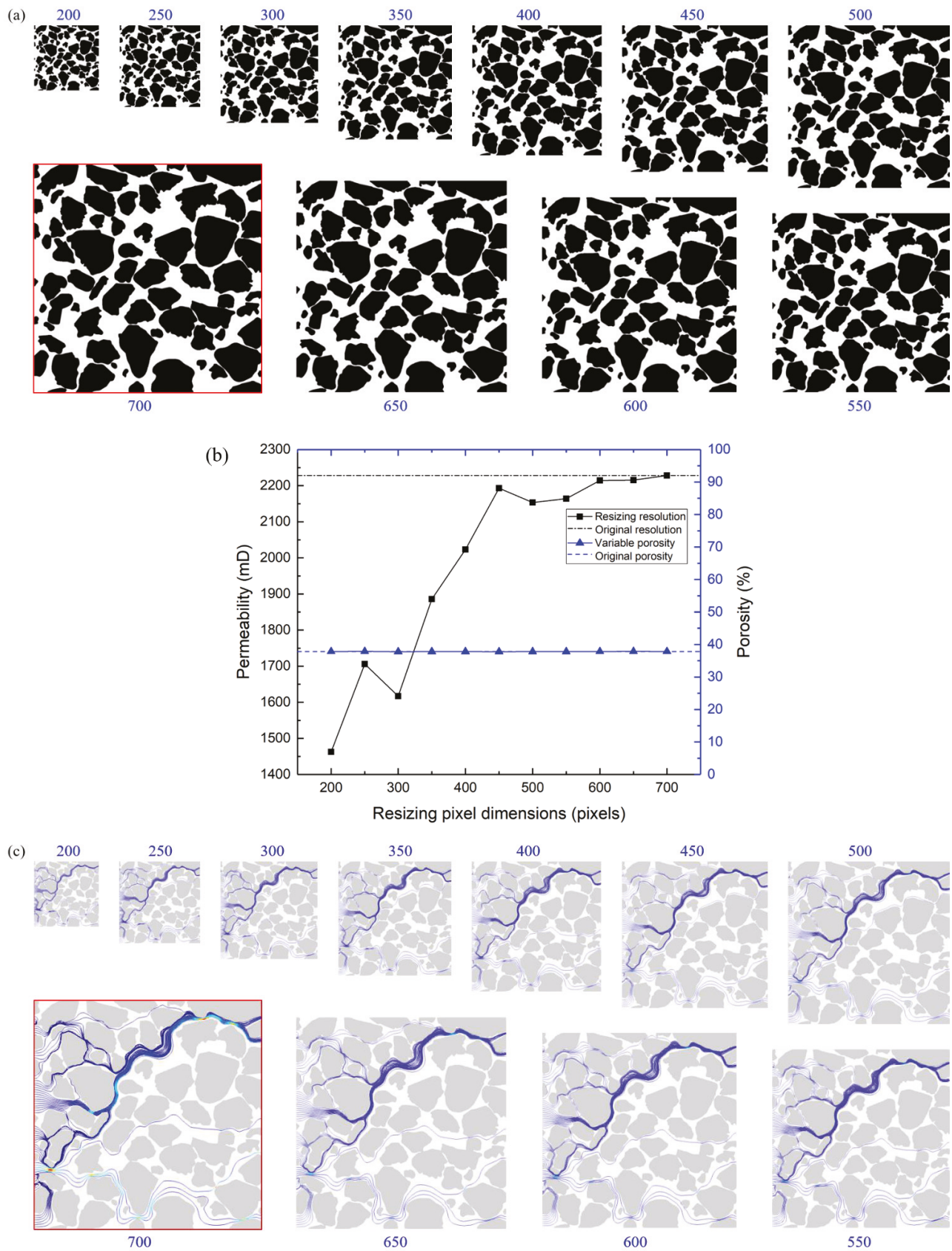


Figure 17. Influence of model resolution on permeability. (a) Pore models with different resolution; (b) porosity and permeability of pore models with different resolution; (c) flow paths and velocity of pore models with different resolution.

4. Discussion

Based on the actual control group of porous sandstone, this paper constructed models that can describe the single parameter variance of grains by mapping and reverse-mapping ideas and by further analyzing the influence of each parameter on the permeability characteristics of pore structure. Basing on actual structure with one single parameter as an influencing factor to analyze the permeability characteristic is of great significance to reveal the permeability mechanism of complex structures.

In this paper, the actual sandstone model is used as the control group. Based on the control single variable principle, the influence of grain radius, space, roundness, orientation, and model resolution on connectivity, porosity, permeability, flow path, and flow velocity. The influences of both grain parameters and the whole model on permeability characteristics are obtained. Compared with the simplified model as the control group, the actual control group ensures the accuracy of permeability characteristics under complex structures. Compared with the analysis of permeability characteristics under multiple groups of actual rock models, the principle of single-variable control ensures the independent regularity between parameter changes and permeability characteristics.

This paper reveals the influence of grain boundary parameters on permeability characteristics on the actual model, but it only shows the laws of changing a single parameter model. In contrast, multiple parameters changing simultaneously are more likely to leads to the difference of natural rocks. Besides, this paper mainly focuses on the two-dimensional model to study the influence of grain parameters on permeability characteristics. However, natural porous rocks exist in a more complex three-dimensional space, and the influence laws of parameters still need to be further verified in three-dimensional models.

Due to the limitations of this study and natural rock characteristics, the study of grain parameter sensitivity of three-dimensional porous rock will explain the permeability laws in natural rocks more truly. In the future, studying the influence of multiple parameter combinations on the seepage characteristics is of great significance to reveal the permeability mechanism under complex porous media.

5. Conclusions

This paper reconstructs models that can describe a single parameter change of grain boundary based on the actual sandstone. Combined with mapping and reverse-mapping ideas, the actual control group and the control of a single variable scientific method were used to analyze the model parameters' influence on permeability characteristics. Firstly, with the increment of the grain radius from -10 to 5 , the porosity and permeability decreased from 56.51 to 28.06% , from $36,635.51$ mD to 14.85 mD, respectively. Secondly, with the multiples of the grain radius from $1/1.08$ to 1.20 , the porosity and permeability increased from 27.13 to 56.49% , from 11.67 mD to $27,723.21$ mD, respectively. Thirdly, with the multiples of the grain roundness from $1/1.8$ to 4.0 , the porosity and permeability increased from 32.55 to 40.87% , from 13.20 mD to 3828.57 mD, respectively. Fourthly, the grain orientation change has less effect on porosity between 37.85 and 43.73% , while it had a strongly random impact on permeability between 0 to 3138.61 mD. Fifthly, with the model resolution increased, the porosity remained unchanged at 37.85% , while permeability shows increased trends and then stabilized from 1462.87 mD to 2228.25 mD.

In conclusion, different grain parameters have significant differences in the influence on permeability characteristics. From the perspective of grain radius, space, and roundness, there is a positive or negative correlation between porosity and permeability. However, there was almost no correlation between porosity and permeability in terms of grain orientation and resolution parameters. The change of model connectivity under different grain parameters directly affects the change of seepage paths. These conclusions can provide a reference for revealing the permeability law between different complex rock structures.

Author Contributions: Conceptualization, H.X.; methodology, R.S. and H.X.; software, H.X. and M.H.; validation, R.S. and C.S.; formal analysis, R.S. and H.X.; resources, C.S.; writing—original draft preparation, R.S. and H.X.; writing—review and editing, H.X.; visualization, R.S., H.X., and M.H.; supervision, L.H.; project administration, L.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors appreciate the reviewers' constructive comments.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Wang, J.; Zhang, Y.; Qin, Z.; Song, S.; Lin, P. Analysis method of water inrush for tunnels with damaged water-resisting rock mass based on finite element method-smooth grain hydrodynamics coupling. *Comput. Geotech.* **2020**, *126*, 103725. [CrossRef]
- Gudala, M.; Govindarajan, S.K. Numerical Modeling of Coupled Fluid Flow and Geomechanical Stresses in a Petroleum Reservoir. *J. Energy Resour. Technol.* **2020**, *142*, 063006. [CrossRef]
- Shi, Y.; Song, X.; Li, J.; Wang, G.; YuLong, F.; Geng, L. Analysis for effects of complex fracture network geometries on heat extraction efficiency of a multilateral-well enhanced geothermal system. *Appl. Therm. Eng.* **2019**, *159*, 113828. [CrossRef]
- Kumari, W.G.P.; Ranjith, P.G.; Perera, M.S.A.; Chen, B.K. Experimental investigation of quenching effect on mechanical, microstructural and flow characteristics of reservoir rocks: Thermal stimulation method for geothermal energy extraction. *J. Pet. Sci. Eng.* **2018**, *162*, 419–433. [CrossRef]
- Bertels, S.P.; DiCarlo, D.A.; Blunt, M.J. Measurement of aperture distribution, capillary pressure, relative permeability, and in situ saturation in a rock fracture using computed tomography scanning. *Water Resour. Res.* **2001**, *37*, 649–662. [CrossRef]
- Jannot, Y.; Lasseux, D. A new quasi-steady method to measure gas permeability of weakly permeable porous media. *Rev. Sci. Instrum.* **2012**, *83*, 015113. [CrossRef] [PubMed]
- Brace, W.; Walsh, J.B.; Frangos, W.T. Permeability of granite under high pressure. *J. Geophys. Res.* **1968**, *73*, 2225–2236. [CrossRef]
- Lin, W. Parametric analyses of the transient method of measuring permeability. *J. Geophys. Res. Solid Earth* **1982**, *87*, 1055–1060. [CrossRef]
- Fheed, A.; Kłodowski, K.; Krzyżak, A. Fracture orientation and fluid flow direction recognition in carbonates using diffusion-weighted nuclear magnetic resonance imaging: An example from Permian. *J. Appl. Geophys.* **2020**, *174*, 103964. [CrossRef]
- Hu, Y.; Wang, Q.; Zhao, J.; Xie, S.; Jiang, H. A Novel Porous Media Permeability Model Based on Fractal Theory and Ideal Grain Pore-Space Geometry Assumption. *Energies* **2020**, *13*, 510. [CrossRef]
- Kang, D.H.; Yang, E.; Yun, T.S. Stokes-Brinkman flow simulation based on 3-D μ -CT images of porous rock using grayscale pore voxel permeability. *Water Resour. Res.* **2019**, *55*, 4448–4464. [CrossRef]
- Zhou, X.P.; Xiao, N. A hierarchical-fractal approach for the rock reconstruction and numerical analysis. *Int. J. Rock Mech. Min.* **2018**, *109*, 68–83. [CrossRef]
- Torquato, S.; Lu, B. Chord-length distribution function for two-phase random media. *Phys. Rev.* **1993**, *47*, 2950–2953. [CrossRef]
- Yin, P.; Zhao, G.F. Stochastic reconstruction of Gosford sandstone from surface image. *Int. J. Rock Mech. Min.* **2014**, *70*, 82–89. [CrossRef]
- Ma, Q.; Chen, Z.; Shi, J.; Li, D. Lattice Boltzmann modeling of VOC desorption and diffusion in porous materials: VOC desorption and diffusion. *Build. Environ.* **2014**, *72*, 145–153. [CrossRef]
- Yang, Y.; Yao, J.; Wang, C.; Gao, Y.; Zhang, Q.; An, S.; Song, W. New pore space characterization method of shale matrix formation by considering organic and inorganic pores. *J. Nat. Gas Sci. Eng.* **2015**, *27*, 496–503. [CrossRef]
- Xiao, H.; He, L.; Li, J.; Zou, C.; Shao, C. Permeability prediction for porous sandstone using digital twin modeling technology and Lattice Boltzmann method. *Int. J. Rock Mech. Min.* **2021**, *142*, 104695. [CrossRef]
- Xiao, H.; He, L.; Li, X.; Zhang, Q.; Li, W. Texture synthesis: A novel method for generating digital models with heterogeneous diversity of rock materials and its CGM verification. *Comput. Geotech.* **2021**, *130*, 103895. [CrossRef]
- Bryant, S.; Cade, C.; Mellor, D. Permeability prediction from geologic models. *AAPG Bull.* **1993**, *77*, 1338–1350.
- Latief, F.D.E.; Fauzi, U. Kozeny–Carman and empirical formula for the permeability of computer rock models. *Int. J. Rock Mech. Min.* **2012**, *50*, 117–123. [CrossRef]
- Mehrizi, A.A.; Farhadi, M.; Sedighi, K.; Delavar, M.A. Effect of fin position and porosity on heat transfer improvement in a plate porous media heat exchanger. *J. Taiwan Inst. Chem. Eng.* **2013**, *44*, 420–431. [CrossRef]

22. Mehrizi, A.A.; Farhadi, M.; Sedighi, K.; Aghili, A.L. Lattice Boltzmann simulation of heat transfer enhancement in a cold plate using porous medium. *J. Heat Transf.* **2013**, *135*, 111006. [CrossRef]
23. Sandstone Image. Available online: <https://www.quora.com/Petroleum-Geoscience-What-is-the-difference-between-effective-porosity-and-porosity> (accessed on 23 April 2021).



Article

A Case Study of Calcium Carbonate Crystallization during Reverse Osmosis Water Desalination in Presence of Novel Fluorescent-Tagged Antiscalants

Konstantin Popov ^{1,*}, Maxim Oshchepkov ^{1,2}, Alexei Pervov ³, Vladimir Golovesov ^{1,3}, Anastasia Ryabova ⁴, Maria Trukhina ¹ and Sergey Tkachenko ^{1,2}

¹ JSC "Fine Chemicals R&D Centre", Krasnobogatyrskaya, Str. 42, b 1, 107258 Moscow, Russia; maxim.os@mail.ru (M.O.); golovesov.vova@mail.ru (V.G.); truheny-mv@yandex.ru (M.T.); s.tkach.8@gmail.com (S.T.)

² Department of Chemistry and Technology of Biomedical Pharmaceuticals, Mendeleev University of Chemical Technology, 125047 Moscow, Russia

³ Department of Water Supply and Sewage, Moscow State University of Civil Engineering, Yaroslavskoe Shosse, 26, 129337 Moscow, Russia; ale-pervov@yandex.ru

⁴ Prokhorov General Physics Institute of the Russian Academy of Sciences, Vavilov Str., 38, 119991 Moscow, Russia; nastya.ryabova@gmail.com

* Correspondence: ki-popov49@yandex.ru

Abstract: Calcium carbonate scaling in reverse osmosis (RO) desalination process is studied in the presence of two novel fluorescent-tagged scale inhibitors 1,8-naphthalimide-tagged polyacrylate (PAA-F1) and 1-hydroxy-7-(6-methoxy-1,3-dioxo-1*H*-benzo[de]isoquinolin-2(3*H*)-yl)heptane-1,1-diyl-bis(phosphonic acid) (HEDP-F) by fluorescent microscopy (FM) and scanning electron microscopy (SEM). Both antiscalants diminished the mean size of calcite crystals relative to the blank experiment. The behavior and localization of HEDP-F and PAA-F1 during calcite scale formation on membrane surface was found to be significantly different from the distribution in similar RO experiments with gypsum, reported earlier. In the former case, both antiscalants are concentrated exactly on the surface of calcium carbonate crystals, while in the latter one they form their own phases (Ca-HEDP-F and Ca-PAA-F1) and are not detected on gypsum scale. The difference is interpreted in terms of interplay between background calcium concentration and sparingly soluble calcium salts' solubility. HEDP-F reveals slightly higher efficiency than PAA-F1 against calcite scale formation, while PAA-F exhibits a higher ability to change calcite morphology. It is demonstrated that there is a lack of correlation between antiscaling efficacy and ability of antiscalant to change calcium carbonate morphology in a particular case study. An application of fluorescent-tagged antiscalants in RO experiments provides a unique possibility to track the scale inhibitor molecules' localization during calcite scale formation. Fluorescent-tagged antiscalants are presumed to become a very powerful tool in membrane scaling inhibition studies.

Keywords: reverse osmosis; membrane fouling; calcium carbonate scaling; fluorescent-tagged polyacrylate; fluorescent-tagged bisphosphonate; fluorescence; scale inhibition

1. Introduction

Reverse osmosis (RO) has become a powerful technology for the purification of sea, brackish and waste water [1–4]. RO is currently the most energy-efficient technology for desalination, with an energy cost of about 1.8 kWh/m³, which is much lower than that of other technologies [3]. However, one of the major limitations in efficient RO application is the surface membrane fouling [4,5]. It is a complex phenomenon and could be a combination of colloidal, organic, inorganic and biofouling [4].

Membrane fouling could significantly reduce productivity and permeate quality. The former leads to increasing operation costs due to increased energy demands, additional

pretreatment, foulants' removal and membrane cleaning and maintenance, as well as reduction in membrane lifetime [3]. Inorganic fouling or scaling is the formation of mineral deposits on the membrane surface as the feed water becomes supersaturated by inorganic salts. The relative content of dissolved salts is increased four to ten times, depending on the operating recovery and rejection efficiencies [4] during high pressure membrane operations. As a result, the concentration of salts may exceed their solubility limit and the salts may crystallize onto membrane surfaces. The most common scales are represented by calcium carbonate, calcium sulfate and silica [2,4,6,7]. Scale formation has always been a serious limitation in designing and operating RO systems since scaling causes flux decline, membrane degradation, loss of production and elevated operating costs.

Scaling was reported to occur by two crystallization pathways, surface crystallization and bulk crystallization [4]. Scale deposition in membrane systems is a combination of these two extreme mechanisms and is affected by membrane morphology and process conditions. Surface crystallization occurs due to the lateral growth of the scale deposit on the membrane surface, resulting in flux decline and surface blockage. Bulk crystallization arises when crystal particles are formed in the bulk phase through homogeneous crystallization and may deposit on membrane surfaces as sediments/particles to form a cake layer that leads to flux decline. In addition, supersaturated scale forming conditions lead to scale growth and agglomeration [4].

To mitigate the risk of membrane scaling, many methods, including feed water pretreatment, the optimization of operational processes, the development of novel membrane materials and the addition of antiscalants, have been developed in accordance with the characteristics of RO operating systems [1,5,8]. An application of antiscalants provides retardation of scale formation, and increases the concentration coefficient of concentrate. It is one of the most commonly applied methods for inhibiting scaling in the RO process, especially in the situation that a high-water recovery is set to reduce concentrate volume but cause an enhanced scaling potential, due to its high efficiency, low cost and easy operation [8].

Among scale inhibitors, polycarboxylates (polyacrylates, polyaspartates, etc.) and phosphonates are found to be highly efficient [2,4,9]. However, in spite of the availability of a good number and wide variety of effective antiscalants, continuous research is being conducted to improve the existing ones [2,9–11]. Recent reviews on scale formation control in RO technologies [2,4,8,9,12] mention hypothetical mechanisms of inhibition: antiscalant molecules adsorb to the active growth sites on the crystal surface of sparingly soluble inorganic salt, formed either in the bulk feeding solution or at the membrane surface. This sorption delays the onset crystallization (nucleation phase of crystallization) or retards the growth of mineral salt crystals (growth phase of crystallization) [4,12].

However, in spite of numerous relevant studies, the lack of understanding of the complicated physicochemical interactions involved among dominant scale-forming substances, antiscalants, membranes and other coexisting substances in solutions still exists [8,11,13,14]. One of the promising possibilities to eliminate some gaps in antiscalant mechanisms understanding is a direct [13,14] or indirect [11] visualization of antiscalant. Indeed, our recent experiments with gypsum scale formation in a laboratory RO facility in the presence of fluorescent-tagged bisphosphonate antiscalant 1-hydroxy-7-(6-methoxy-1,3-dioxo-1*H*-benzo[de]isoquinolin-2(3*H*)-yl)heptane-1,1-diyl-bis(phosphonic acid), HEDP-F (H₄hedp-F) [13] and of fluorescent 1,8-naphthalimide-tagged polyacrylate (PAA-F1) [14] revealed a paradoxical effect: an antiscalant does not show any interaction with gypsum at all, but provides nevertheless retardation of corresponding deposit formation.

Thus, it was of particular interest to track both fluorescent scale inhibitors during calcite deposition on RO membranes in a model experiment. The present study is focused therefore on the scale inhibitor visualization after RO treatment of a model water sample with high calcium carbonate content in the presence of two different fluorescent antiscalants—PAA-F1 and HEDP-F (Figure 1). One of them represents polycarboxylates (PAA-F1), while another one represents organophosphonic acids (HEDP-F). The major

objective of the present work was to model the naturally occurring calcium carbonate supersaturation process as the feeding solution steadily gets saturated, and to ascertain the scale inhibitor location. As far as we know, this is a first full-scale report on antiscalant's visualization during calcite fouling onto membrane surface in a RO experiment.

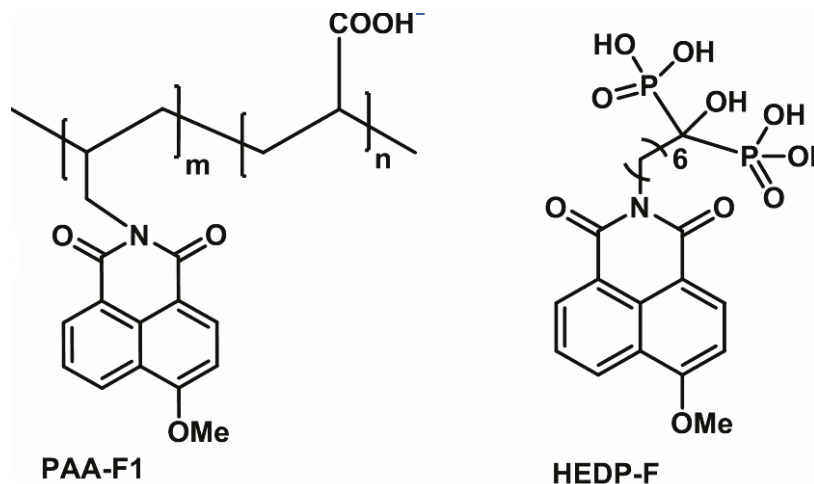


Figure 1. PAA-F1 and HEDP-F molecular structures.

2. Materials and Methods

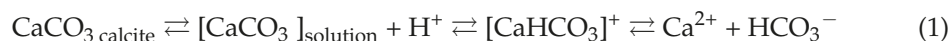
2.1. Reagents

Antiscalant PAA-F1 (Figure 1) was synthesized by our group, as described elsewhere [15]. It has the mean molecular mass 4000 Da with c.a. 1 mass % of fluorescent 1,8-naphthalimide moiety. This corresponds randomly to c.a. 0.2 fluorescent fragments per one molecule of polyacrylate. HEDP-F (molecular mass 502.1 Da), (Figure 1), was synthesized by our group as described in [16]. For model scaling solutions, reagent grade $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and Na_2CO_3 were used in crystalline form and were separately dissolved in distilled water (conductivity 2 $\mu\text{S}/\text{cm}$) to prepare stock solutions.

2.2. Calcium Carbonate Feed Solutions Preparation

Following this study objectives, we had to start experimental runs with feeding aqueous solution, undersaturated relative to calcium carbonate. At the same time, at the end of each run the retentate has to become supersaturated, and capable of generating a sufficient amount of calcite crystals for scanning electron microscope (SEM) detection, and for confocal luminescent microscope analysis (FM) in both antiscalant-injected and blank experiments. Thus, the dosage of antiscalant should not be too high in order not to suppress scaling completely.

The solubility of calcite in water at 25 °C and zero ionic strength (*I*) corresponds to 0.058 $\text{mmol} \cdot \text{dm}^{-3}$ [17]. However, at pH below 10 a higher concentration of calcium and carbonate ions in aqueous phase becomes possible due to HCO_3^- anions formation:



In order to find optimal experimental conditions, the chemical speciations for calcium have been performed, based on chemical equilibria data [17–20], operating SPECIES software [21], (Table 1, Table 2 and Figure 2).

Table 1. Equilibrium constants ($\log K$), used for equilibrium speciations at 25 °C and $I = 0$.

Equilibrium	$\log K (-\log K_{\text{sol}})$	Reference
$\text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_3 \text{ calcite}$	8.485	[18]
$\text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons [\text{CaCO}_3]_{\text{solution}}$	3.22	[17]
$\text{H}^+ + \text{CO}_3^{2-} \rightleftharpoons \text{HCO}_3^-$	10.34	[19]
$\text{H}^+ + \text{HCO}_3^- \rightleftharpoons \text{H}_2\text{CO}_3$ *where $[\text{H}_2\text{CO}_3] = [\text{CO}_2(\text{aq})] + [\text{H}_2\text{CO}_3]$	6.36	[19]
$\text{Ca}^{2+} + \text{HCO}_3^- \rightleftharpoons \text{CaHCO}_3^+$	1.14	[20]

Table 2. Calcium species' distribution as a function of pH at 25 °C and $I = 0 \text{ mol dm}^{-3}$.

pH	Calcium Species, % (mol)			
	Ca^{2+}	$\text{CaCO}_3 \text{ solution}$	$[\text{CaHCO}_3]^+$	$\text{CaCO}_3 \text{ calcite}$
	Initial solution $[\text{Ca}^{2+}] = 2.5 \text{ mmol} \cdot \text{dm}^{-3}$; $[\text{HCO}_3^-] = 2.5 \text{ mmol} \cdot \text{dm}^{-3}$			
7.00	97.2	0.15	2.65	0.0
7.12	97.0	0.20	2.77	0.0
7.16	95.9	0.22	2.73	1.19
7.20	91.0	0.22	2.49	6.29
7.40	70.6	0.22	1.57	27.62
7.80	43.4	0.22	0.63	55.71
8.00	34.3	0.22	0.40	65.08
9.00	11.0	0.22	0.04	88.78
The same solution, concentrated (6-fold)				
6.00	94.4	0.03	5.60	0
6.08	87.7	0.04	5.48	6.78
6.20	70.1	0.04	4.16	25.73
6.80	26.2	0.04	1.04	72.69
7.00	19.8	0.04	0.66	79.52
8.00	5.7	0.04	0.07	94.18

The data, presented in Table 2 and in Figure 2a, demonstrate that the initial $2.5 \text{ mmol} \cdot \text{dm}^{-3}$ calcium carbonate solution has no solid phase below pH 7.1, while above this boundary calcite should appear in significant amounts, reaching 95 mol % at pH 10. For more concentrated calcium carbonate solutions ($15 \text{ mmol} \cdot \text{dm}^{-3}$) the boundary of heterogeneity is shifted to more acidic solutions (Figure 2b). Thus, if $2.5 \text{ mmol} \cdot \text{dm}^{-3}$ calcium carbonate solution is prepared at pH 7.1, it would be a homogeneous liquid phase with 1% confidence. A six-fold saturation of this solution in a RO facility at the same pH should lead to the formation of solid phase (calcite), which would accumulate no less than 79 mol % of total calcium, present in retentate (Figure 2b). Following these speciation diagrams the stock $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and Na_2CO_3 solutions have been prepared in such concentrations, and with such pH, that being mixed in 1:1 volume ratio they would give a $2.5 \text{ mmol} \cdot \text{dm}^{-3}$ calcium carbonate solution at pH 7.9, that is above the saturation level: 1.5 mmol calcite (60%) has to be formed at this pH value. Notably, the supersaturation (S) of initial $2.5 \text{ mmol} \cdot \text{dm}^{-3}$ CaCO_3 solution is ranging from 2.5 (pH 7.9) to 5.0 (pH 8.4) according to diagram at Figure 2a. Here S is denoted as $[\text{Ca}_{\text{init}}]/[\text{Ca}_{\text{equil}}]$, where $[\text{Ca}_{\text{init}}]$ indicates initial calcium concentration, and $[\text{Ca}_{\text{equil}}]$ indicates equilibrium calcium concentration according to the diagram at Figure 2a. However, due to the slow kinetics of solid phase formation, the initial feed solution remains homogeneous after $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and Na_2CO_3 solutions

get mixed. Meanwhile, the higher initial pH provides a higher yield of calcite crystals at the end of an experiment.

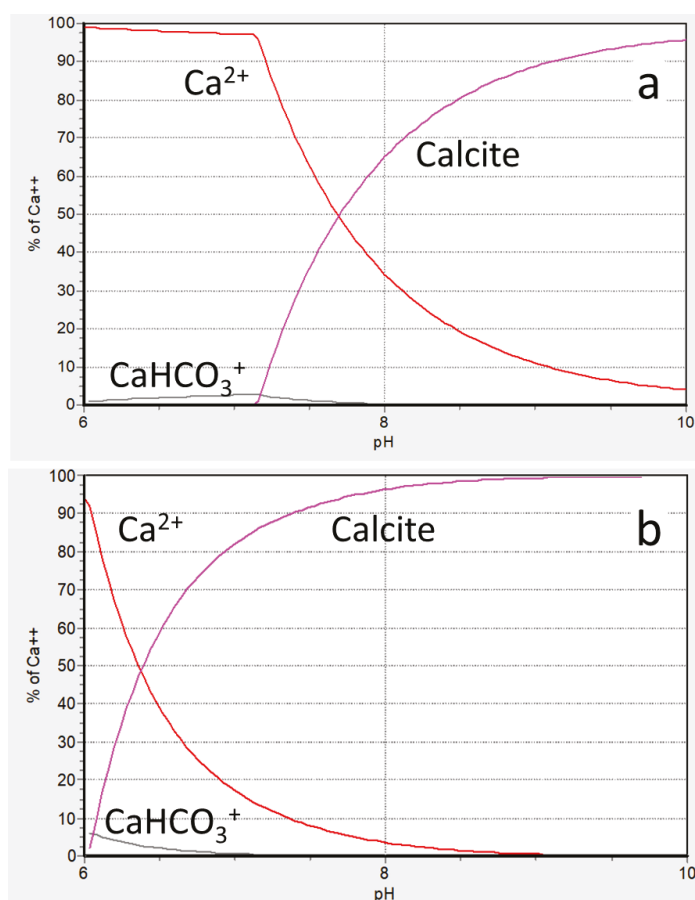


Figure 2. Chemical speciations for 0.25 (a) and 1.2 (b) mmol·dm^{−3} CaCO₃ as a function of pH at 25 °C and *I* = 0 mmol·dm^{−3}.

Each stock solution was filtered (200 nm; Hydrophilic PTFE Millipore Millex-LG membrane) before mixing to remove dust particles. An antiscalant was added to the feed solution before use to achieve 5 mg·dm^{−3} dosage. This corresponds to c.a. 0.07 mmol·dm^{−3} PAA-F1 concentration (−CH₂CH<^{COOH} fragments) and to 0.01 mmol·dm^{−3} HEDP-F concentration.

2.3. Reverse Osmosis Membrane System

Calcite scaling experiments were carried out using an automatically controlled laboratory-scale cross-flow RO spiral wound module RE 1812 tailored with thin film composite BLN membrane (Figure 3). The test unit was operated in circulation mode whereby concentrate after membrane module was returned back to feed water tank. The feed water was added to feed water tank 1. The volume of tank 1 was 5 L. Feed water from tank 1 was supplied by small gear pump 2 to membrane module 3. In all the experiments capacities were used comprising commercially available spiral-wound filter elements (CSM RE1812-80 GPD) made of polyamide and manufactured by CSM (Korea) operated at constant feed flow rate of 72 ± 0.2 dm³/h, permeate flow rate of 6.0–6.3 dm³/h, constant temperature of 25.0 ± 1 °C; constant pressure 7 ± 0.2 bar in concentration mode. The area of membrane surface was 0.5 m².

Stabilized salt rejection, at a constant pressure of 7 bar, solution temperature of 25 °C, and a pH value of 6.5–7.0 is reported to be 96.5–97.0 % for a 200 mg·dm^{−3} NaCl solution

(manufacturer's data). Each run was performed with a virgin membrane sample. Flux recovery was 80 to 83%.

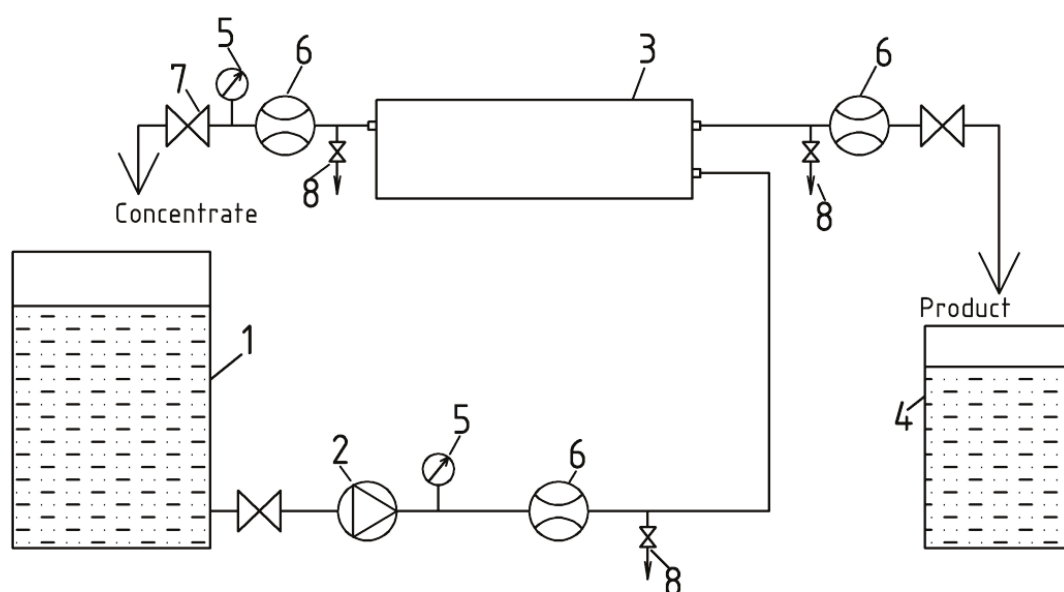


Figure 3. Schematic diagram of laboratory RO unit for membrane scaling tests: 1—feed water tank; 2—pump; 3—spiral wound membrane module; 4—permeate tank; 5—pressure gauge; 6—water flow meter; 7—concentrate flow adjusting valve; 8—sampler.

2.4. Calcium Carbonate Scaling Experiments

Individual calcite scaling experiments were performed with a virgin sample of a pre-soaked membrane: each membrane contacted with distilled water overnight (12–14 h) to allow membrane permeability to stabilize. Experiments were run with a single superficial cross-flow velocity and were terminated after reaching concentration coefficient $K = 6$. The cross-flow velocity varied from 3.0 to 3.6 cm/s. This value adequately fits the range of cross-flow velocities encountered in spiral-wound RO/NF. The retentate was periodically sampled and tested for calcium content (EDTA titration) and pH. Pressure and retentate cross-flow rates were monitored through digital sensors. The permeate volume was continuously recorded. The temperature was almost constant (varying by less than 1 °C) during each experiment at a level of 25 °C.

At the end of each experimental cycle, scaled membrane samples were carefully extracted from the autopsied membrane element and submerged into an ultrapure water bath for approximately 2 s to prevent further crystallization from evaporation of residual scaling solution. Membrane samples were then air dried for at least 48 h and afterwards cut into ten equally sized 4 cm × 10 cm pieces. These pieces were stored in desiccators for at least 24 h. Then the fragments were sent for analysis by scanning electron microscopy (SEM) and by fluorescent microscopy (FM).

2.5. Fluorescent Microscopy Measurements

Confocal microscopy measurements have been run with laser scanning confocal microscope LSM-710-NLO (Carl Zeiss Microscopy, Jena, Germany), 20× Plan-Apochromat objective (NA = 0.8). The membrane samples were placed onto a Petri dish with a glass bottom 0.16 mm thick. The fluorescence was recorded in the wavelength range of 470–600 nm, when excited by laser radiation with a wavelength of 458 nm. It should be noted that 1,8-naphthalimide-based antiscalants provide fluorescence in the blue spectral region. However, the fluorescent channel can be assigned any pseudo-color in the digital image when acquired by laser scanning microscopy. Most often the fluorescent channel, if it is a single one, is assigned the green pseudo-color because the dynamic range of human color

perception for green is much wider than for blue. Thus, in the present work the original blue emission is changed for an artificial green pseudo-color. In some cases, an overlay of the fluorescent images with distribution of PAA-F1 and HEDP-F (green pseudo-color in images) and transmitted light image (grey color) was obtained.

2.6. SEM Crystal Characterization

The membrane pieces with precipitated solids, after being triply rinsed with deionized water and air dried at 20–25 °C, were characterized by scanning electron microscopy (SEM, Hitachi TM-3030, Tokyo, Japan). The sample examinations by SEM were done at 15 kV accelerating voltage in a Charge-Up Reduction Mode with crystal phase located on Conducting Double-Sided Tape and 4.1 mm working distance.

3. Results and Discussion

3.1. Variation of Calcium Concentration in Retentate

The data on calcium concentration in a blank experiment reveal a notable deviation from linearity (dashed line) for concentration coefficient $K = 2$ (Figure 4). This indicates accumulation of Ca^{2+} ions in solid phase. The difference between the total calcium content (retentate + membrane; dashed line) and its concentration in the liquid phase (Figure 4c) increases steadily as K values are changing from 3 to 6. Thus, almost 30% of calcium gets deposited as calcite at the end of experiment, while for $K < 2$ all calcium species are found in a liquid phase. At the same time, pH values remain constant within the range $7.9 \div 8.5$ (Table 3).

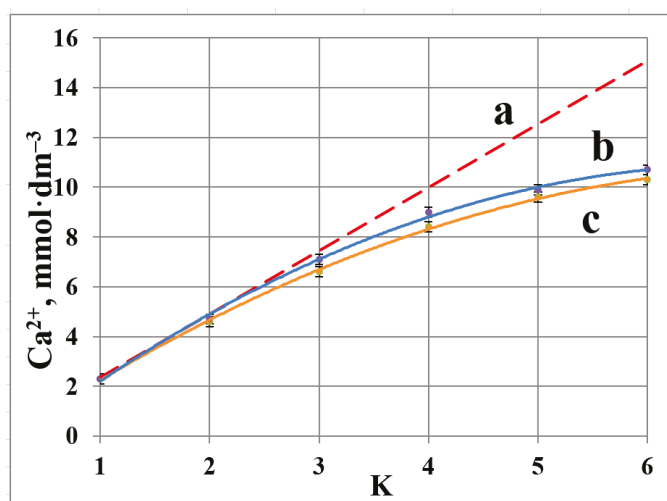


Figure 4. Variation of total calcium content in retentate + membrane (a); of calcium concentration in retentate in presence of HEDP-F (b); and in retentate in a blank run (c).

Table 3. Variation of calcium concentration and pH in retentate.

K	Blank Experiment		In Presence of PAA-F1, 5 $\text{mg}\cdot\text{dm}^{-3}$		In Presence of HEDP-F, 5 $\text{mg}\cdot\text{dm}^{-3}$	
	pH	Ca^{2+} , $\text{mmol}\cdot\text{dm}^{-3}$	pH	Ca^{2+} , $\text{mmol}\cdot\text{dm}^{-3}$	pH	Ca^{2+} , $\text{mmol}\cdot\text{dm}^{-3}$
1	7.9	2.4 ± 0.1	8.2	2.5 ± 0.1	8.4	2.5 ± 0.1
2	8.5	4.6 ± 0.1	8.6	5.6 ± 0.1	8.3	5.5 ± 0.1
3	8.4	6.6 ± 0.1	8.5	7.2 ± 0.2	8.3	7.4 ± 0.1
4	8.3	8.4 ± 0.1	8.5	8.5 ± 0.1	8.3	9.0 ± 0.1
5	8.1	9.6 ± 0.1	8.5	9.5 ± 0.1	8.1	9.9 ± 0.1
6	8.0	10.3 ± 0.1	8.4	10.9 ± 0.1	8.0	10.6 ± 0.1

Notably, calcite deposition on membrane surface (30%) appears to be less than the expected equilibrium value (95%). This difference is attributed partly to the uncompleted equilibrium state of the system and partly to the loss of some carbonate ions in the form of CO_2 (some bubbles have been detected in permeate).

An incorporation of antiscalant diminishes scale deposition for $K = 2$ and 3 , indicating a definite scale inhibition phenomenon. However, at $K = 6$ a $5 \text{ mg} \cdot \text{dm}^{-3}$ dosage fails to retard scaling, and the corresponding “b” and “c” curves demonstrate similar values for both HEDP-F and PAA-F1, Figures 4 and 5. At the same time, HEDP-F reveals a better antiscaling performance relative to PAA-F1 at $K = 2$ and $K = 3$. This is in reasonable agreement with static tests, run for the non-fluorescent analogues of HEDP-F and PAA-F1: HEDP and PAA [22–24].

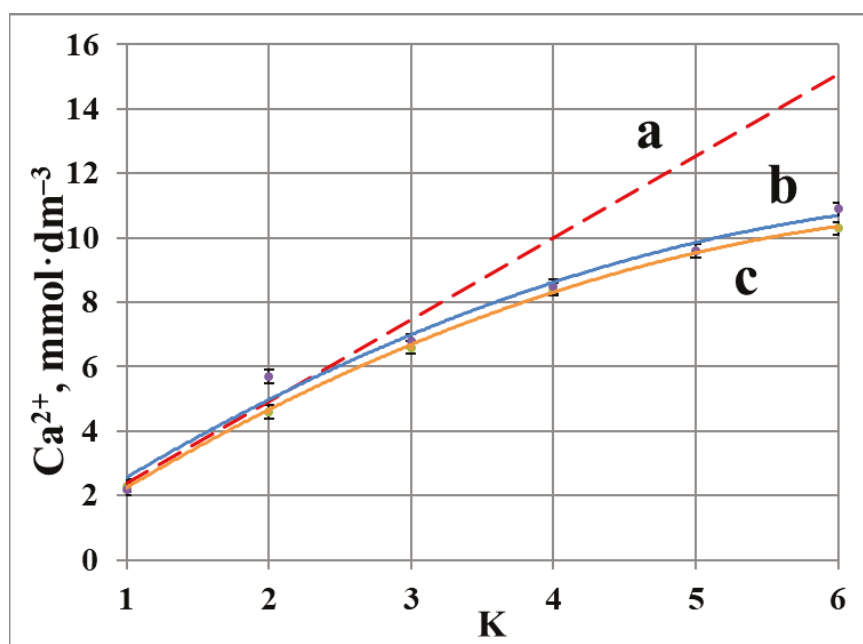


Figure 5. Variation of total calcium content in retentate + membrane (a); of calcium concentration in retentate in the presence of PAA-F1 (b); and in retentate in a blank run (c).

3.2. SEM and FM Analysis of Membrane Surface

SEM images of RO membrane surface after a blank run (Figure 6) demonstrate a small number of isolated crystals and crystal clusters, typical for calcite [4,22]. Along with large aggregates with sizes around 20 to 30 μm , Figure 6c, there is also a fine fraction (sizes 500 nm and less) (Figure 6d). On the whole, the calcium carbonate phase covers much less than 1% of membrane surface.

After RO experiment with HEDP-F, calcium carbonate crystals reveal less uniform distribution on the membrane’s surface (Figure 7a), and a smaller mean size relative to the blank experiment: c.a. 10 μm , Figure 7b–d. However, some particle aggregates with sizes around 50 μm are also detected. The morphology of crystals does not seem to change significantly.

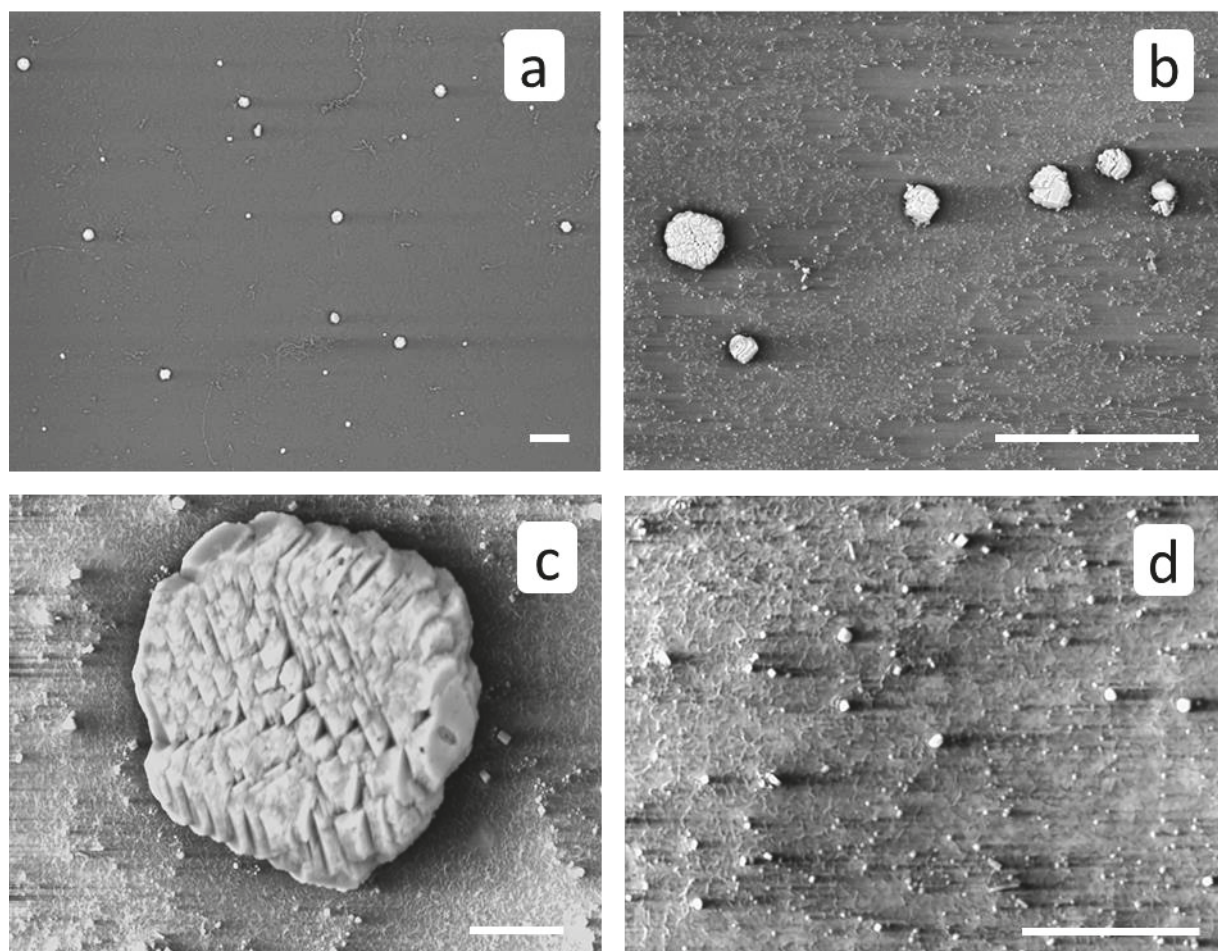


Figure 6. SEM images of RO membrane surface after a blank run. Scale marker corresponds to 100 μm (a,b) or to 10 μm (c,d).

Virgin membrane surface exhibits a weak fluorescence itself (Figure 8a), but this fluorescence does not mask antiscalant (Figure 8b). Fluorescent images of membrane surface after RO treatment in the presence of HEDP-F demonstrate, that antiscalant is concentrated exactly on the surface of calcium carbonate crystals, Figures 8b and 9. Notably, an “inside” location of HEDP-F is normally visible as a shining crystal center with a dark crystal surface [13,16]. Although, one can’t exclude an antiscalant presence in the form of traces (which are beyond the detection limits) inside the crystals, but this effect is definitely negligible relative to dominating fluorescence exactly on the calcite surface. A dominant location of HEDP-F on calcite surface is very much different from its distribution, observed by us earlier in a similar RO experiment with gypsum [13]. In the case of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ scale formation HEDP-F is completely accumulated in its own solid phase (Ca-HEDP-F), but it was not detected on gypsum crystals at all. At the same time, HEDP-F distribution on CaCO_3 surface is not uniform: some crystals are covered by an antiscalant completely, some have accumulated HEDP-F only at the edges, and some reveal either traces of fluorescent marker or even the lack of its presence (Figure 9c). Meanwhile, Figure 9c indicates also some small green spots on the membrane surface, which can be attributed either to Ca-HEDP-F solids or to HEDP-F, unevenly adsorbed directly to the membrane surface.

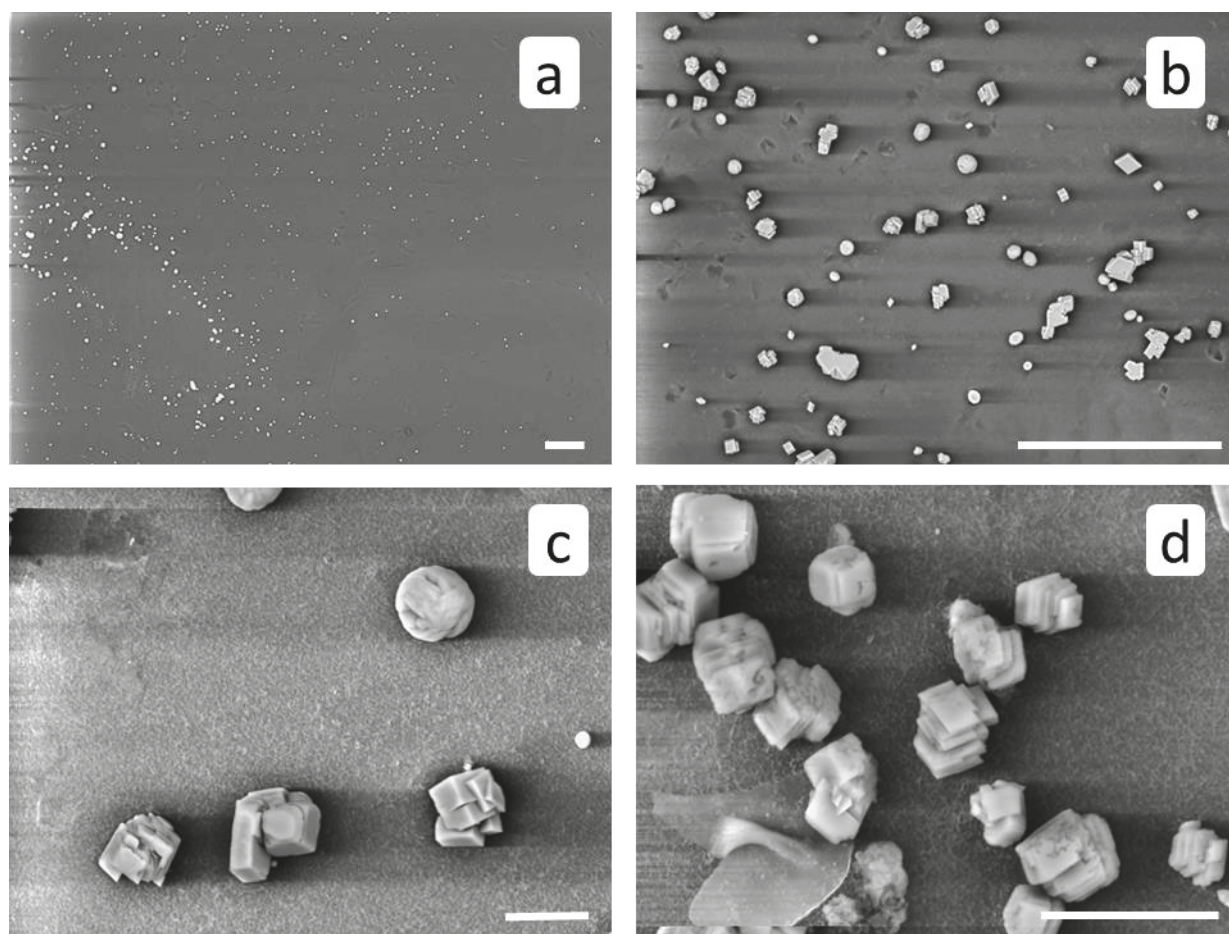


Figure 7. SEM images of membrane surface after RO treatment in the presence of HEDP-F. Scale marker corresponds to 100 μm (a,b) or to 10 μm (c,d).

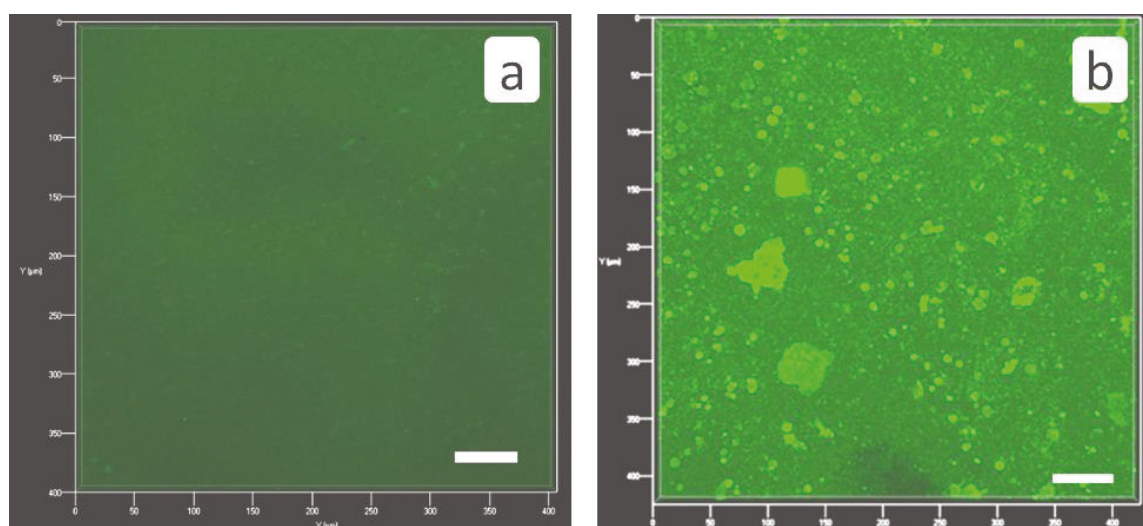


Figure 8. 3D fluorescent images of virgin untreated membrane (a); and of membrane surface after RO treatment in the presence of HEDP-F (b). HEDP-F fluorescence—green pseudo-color, Scale marker corresponds to 50 μm .

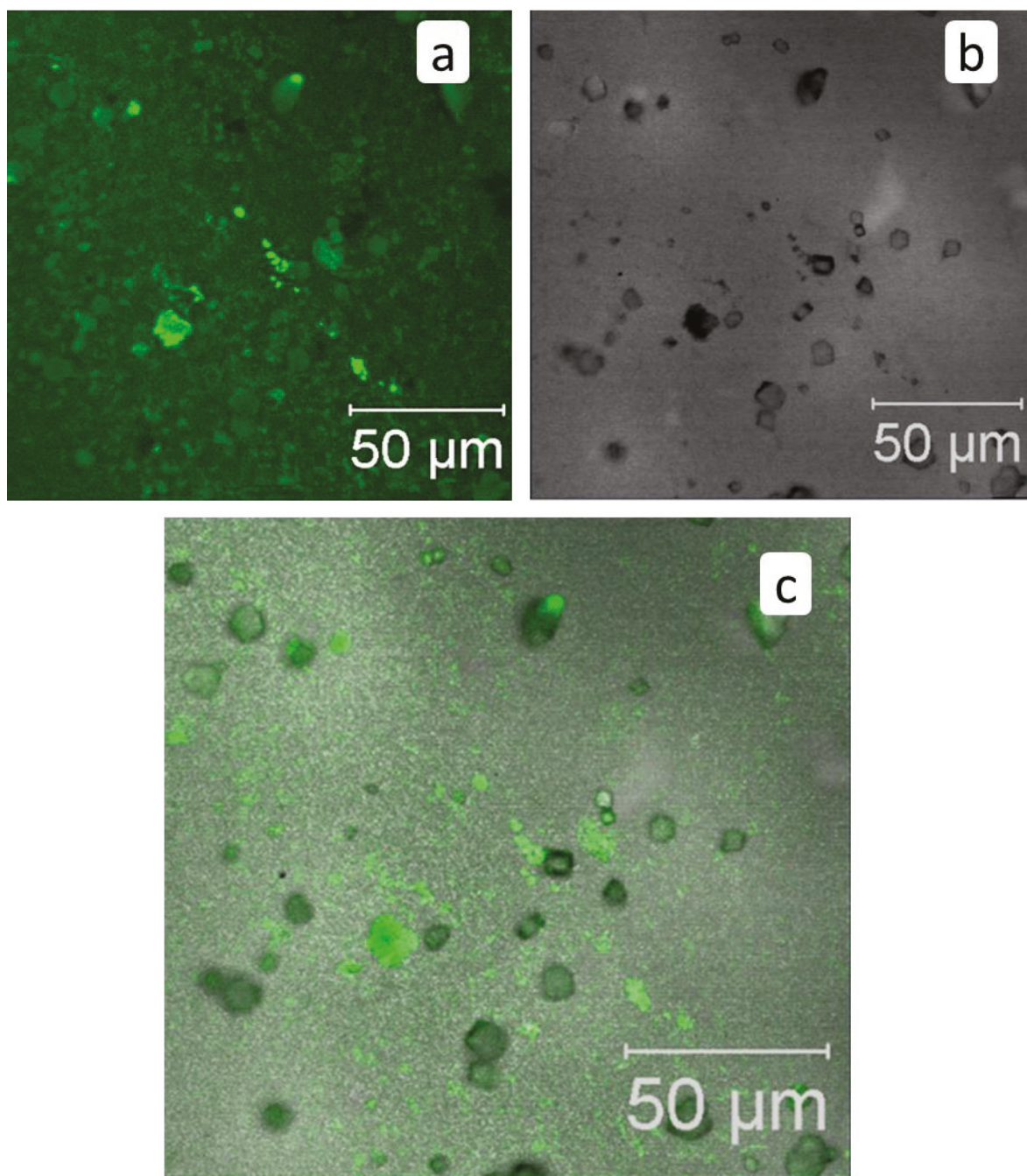


Figure 9. Fluorescent images of membrane surface after RO treatment in presence of HEDP-F: **a**—HEDP-F fluorescence—green pseudo-color, **b**—transmitted light image (grey color), **c**—imposition of **a,b** channels.

Tentatively, the differences in HEDP-F location between RO experiments with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaCO_3 scaling are associated with initial (Ca^{2+}) concentration, and with $\text{Ca}/\text{HEDP-F}$ mole ratio. In gypsum scaling experiments the calcium content was adjusted to $15 \text{ mmol} \cdot \text{dm}^{-3}$, and $0.014 \text{ mmol} \cdot \text{dm}^{-3}$ HEDP-F dosage was used [13]. In the recent study, all experiments started with $[\text{Ca}^{2+}] = 2.5 \text{ mmol} \cdot \text{dm}^{-3}$, while HEDP-F dosage was almost the same as in [13]: $0.01 \text{ mmol} \cdot \text{dm}^{-3}$. Thus, in a gypsum scaling experiment most of antiscalant was accumulated in Ca-HEDP-F phase long before retentate got supersaturated relative to $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. This fact was well documented by FM measurements of liquid phase [13]. We can't rule out the possibility of Ca-HEDP-F phase formation in the present study. These

are normally observed as spherical green species [14,16]. However, a confident assignment of green spots on membrane surface (Figure 9c) to solid Ca-HEDP-F particles is hardly possible, as far as visually they look similar to fine particles of calcite. On the other hand, a significant part of 25 mg of HEDP-F, present in 5 L of stock solution, is adsorbed on macro-crystals of CaCO_3 as a surface layer. Thus, a very little amount, if any, is left for a separate Ca-HEDP-F phase formation.

At the same time, the relative rates of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, CaCO_3 and Ca-HEDP-F formation at equal supersaturation may also become responsible for the observed differences. Besides, a different sorption ability of HEDP-F on CaCO_3 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ surfaces at pH $7 \div 8$ may also give some contribution to these differences.

At first glance, the data presented in Figures 4 and 7–9, prove the conventional mechanism of inhibition: antiscalant molecules adsorb at the CaCO_3 crystal surface active growth sites, and retard crystal growth and aggregation [12]. Indeed, the mean size of calcite crystals, deposited in presence of HEDP-F, is smaller than that one in a blank experiment. Besides, FM indicates a nonuniform localization of HEDP-F on some calcite particles with higher accumulation of antiscalant exactly on the crystal edges and faces. On the other hand, the sizes of antiscalant-covered and uncovered calcite crystals (Figure 9c) are almost the same. This fact indicates, that the sorption of HEDP-F on the surface of already formed CaCO_3 plays the secondary role (if any) in retardation of scale deposition. Thus, a nonconventional mechanism, reported by us earlier for gypsum [13,14,19], can also be applied in this particular case. It was proposed that antiscalant molecules block not the nuclei of sparingly soluble salt and the surface of its macrocrystals, but the surface of solid nano/micro impurities, that are always present in any aqueous solution, even after its filtration with 200 nm pore membranes [25–27]. These nano/micro impurities (nanodust) act as promoters of heterogeneous nucleation of sparingly soluble salts. Their blockage by antiscalant molecules diminishes the number of crystallization centers, available for calcite nucleation, and causes retardation of initial (nucleation) steps of scale formation. As a result, calcite solution in presence of antiscalant becomes more supersaturated than the blank one. This in turn leads to the formation of smaller sized crystals.

The RO experiment with PAA-F1 (Figures 10 and 11) demonstrates the same effect as with HEDP-F. The mean size of deposited crystals (Figure 10a) is smaller than of those, formed in a blank experiment (Figure 6a). Antiscalant is also accumulated mostly on calcite crystals (Figure 11a). Meanwhile, in the case of calcite PAA-F1, it also demonstrates behavior different to gypsum scale formation [14]. In RO experiments with gypsum, PAA-F1, like HEDP-F, does not interact with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals, but forms individual solid phase Ca-PAA-F1.

At the same time, unlike HEDP-F, polyacrylate definitely causes a well-expressed crystal morphology change of calcium carbonate (Figure 10d). Although such effects have been registered earlier both in our experiments [28], and in experiments of other research groups [29,30], this observation should still be noted. The less efficient antiscalant PAA-F1 causes morphology change of calcite, while the more efficient HEDP-F does not. This result casts doubt on the validity of the conventional statement, that the crystal habit change by molecules of antiscalant is an approval of its scale inhibition activity [12]. Current observation gives an additional indication that a correlation between antiscalant's efficacy and its ability to change scale crystal habit is generally missing.

A comparison of HEDP-F and PAA-F1 distribution onto calcite surface also reveals some differences. PAA-F1 covers the CaCO_3 surface completely and rather uniformly, while HEDP-F demonstrates a nonuniform location: some crystals of calcium carbonate appear to be completely uncovered, some are partly covered, while some are covered completely. The present study indicates, along with latest reports [27,31], that fluorescent-tagged scale inhibitors are capable to provide valuable information on the nature of scale inhibition.

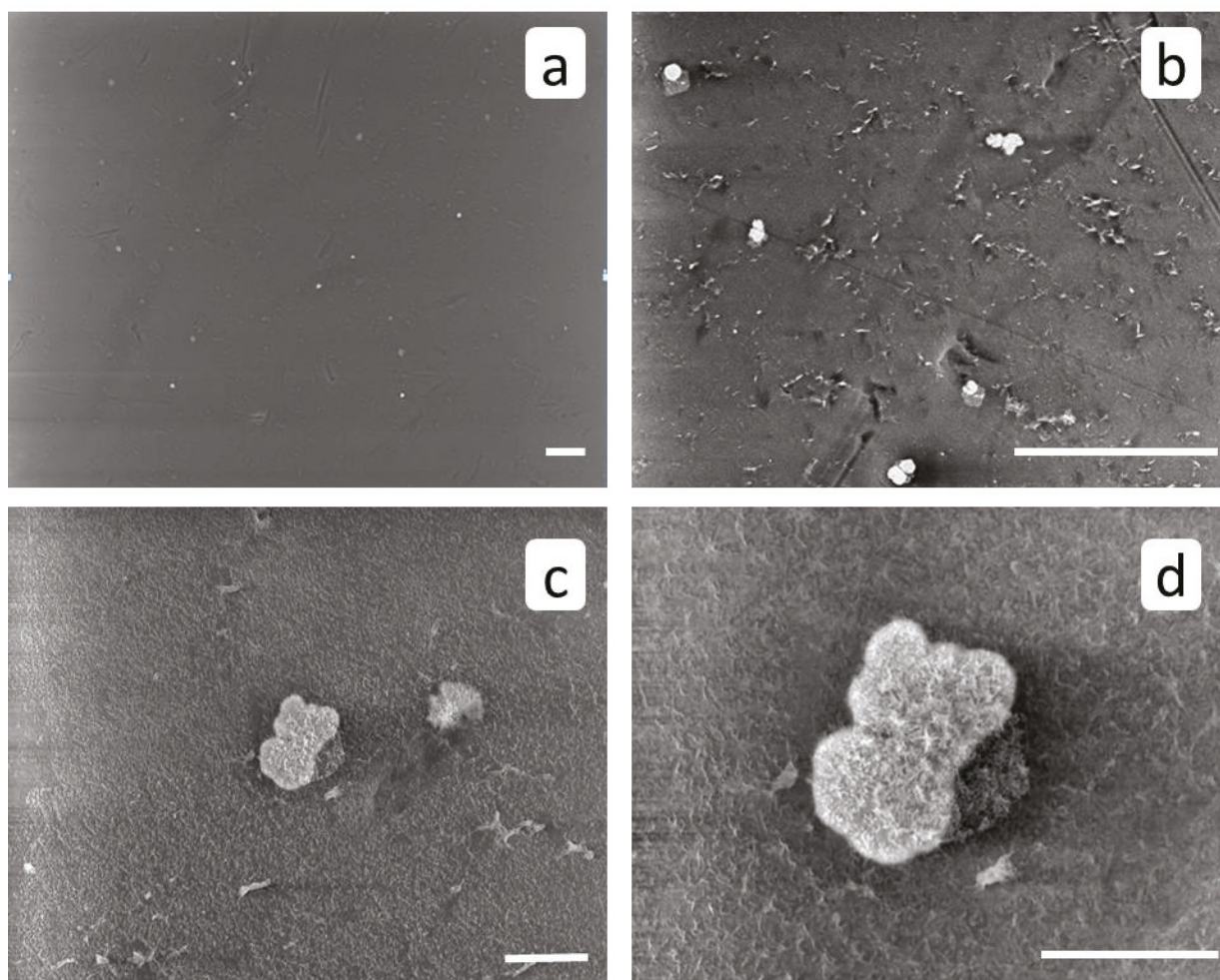


Figure 10. SEM images of membrane surface after RO treatment in presence of PAA-F1; Scale marker corresponds to 100 μm (a,b); or to 10 μm (c,d).

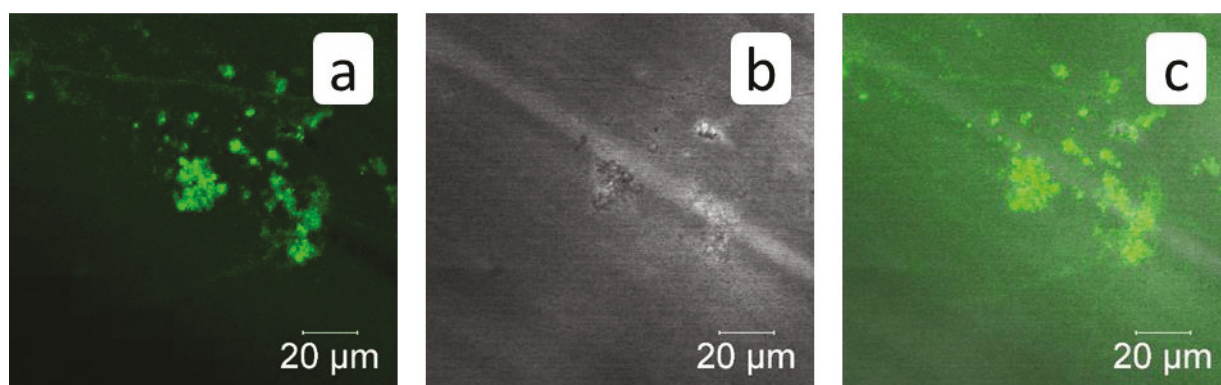


Figure 11. Fluorescent images of membrane surface after RO treatment in the presence of PAA-F1. (a)—PAA-F1 fluorescence—green pseudo-color; (b)—transmitted light image (grey color); (c)—imposition of (a,b) channels.

4. Conclusions

It is found that the behavior and localization of HEDP-F and PAA-F1 during calcite scale formation on membrane surface is very different from their distribution in similar RO experiments with gypsum. In the former case both antiscalants are concentrated exactly on the surface of calcium carbonate crystals, while in the latter case they form their own

phases: Ca-HEDP-F and Ca-PAA-F1. The difference is interpreted in terms of interplay between background calcium concentration and sparingly soluble calcium salts solubility.

HEDP-F and PAA-F1 reveal different distribution onto calcite surface: PAA-F1 covers the CaCO_3 surface completely and rather uniformly, while HEDP-F demonstrates uneven location.

The lack of correlation between the efficacy of the antiscalant and its ability to change the morphology of the calcium carbonate in the particular case study has been demonstrated.

The utility of chemical speciations for the preliminary choice of calcium carbonate solutions (pH, initial concentration) is shown.

An application of fluorescent-tagged antiscalants in RO experiments provides a unique possibility to track the scale inhibitor molecules' location during calcite scale formation.

Author Contributions: Conceptualization, K.P. and A.P.; methodology, A.P., K.P. and A.R.; software, M.T.; investigation, V.G. (RO experiments), M.O. (synthesis of antiscalants), S.T. (SEM), A.R. (FM) and M.T. (speciations); resources, M.O.; data curation, M.O.; writing—original draft preparation, K.P.; writing—review and editing, A.P. and S.T.; visualization, M.O.; supervision, M.O.; project administration, M.O.; funding acquisition, M.O. All authors have read and agreed to the published version of the manuscript.

Funding: The authors would like to thank Russian Science Foundation, Project No. 19-79-10220 for the financial support of the present study.

Institutional Review Board: Not applicable.

Acknowledgments: This work was carried out with the using equipment of the Center for Collective Use No. 74834 "Technological and diagnostic center for the production, research and certification of micro and nanostructures" in GPI RAS.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Anis, S.F.; Hashaikeh, R.; Hilal, N. Reverse osmosis pretreatment technologies and future trends: A comprehensive review. *Desalination* **2019**, *452*, 159–195. [CrossRef]
2. Matin, A.; Rahman, F.; Shafi, H.Z.; Zubair, S.M. Scaling of reverse osmosis membranes used in water desalination: Phenomena, impact, and control; future directions. *Desalination* **2019**, *455*, 135–157. [CrossRef]
3. Jiang, S.; Li, Y.; Ladewig, B.P. A review of reverse osmosis membrane fouling and control strategies. *Sci. Total Environ.* **2017**, *595*, 567–583. [CrossRef]
4. Antony, A.; Low, J.H.; Gray, S.; Childress, A.E.; Le-Clech, P.; Leslie, G. Scale formation and control in high pressure membrane water treatment systems: A review. *J. Membr. Sci.* **2011**, *383*, 1–16. [CrossRef]
5. Goh, P.S.; Lau, W.J.; Othman, M.H.D.; Ismail, A.F. Membrane fouling in desalination and its mitigation strategies. *Desalination* **2018**, *425*, 130–155. [CrossRef]
6. Demadis, K.D.; Neofotistou, E.; Mavredaki, E.; Tsiknakis, M.; Sarigiannidou, E.-M.; Katarachia, S.D. Inorganic foulants in membrane systems: Chemical control strategies and the contribution of green chemistry. *Desalination* **2005**, *179*, 281–295. [CrossRef]
7. Liu, Q.; Xu, G.-R.; Das, R. Inorganic scaling in reverse osmosis (RO) desalination: Mechanisms, monitoring, and inhibition strategies. *Desalination* **2019**, *468*, 114065. [CrossRef]
8. Yu, W.; Song, D.; Chen, W.; Yang, H. Antiscalants in RO membrane scaling control. *Water Res.* **2020**, *183*, 115985. [CrossRef]
9. Mazumder, J.M.A. A review of green scale inhibitors: Process, types, mechanism and properties. *Coatings* **2020**, *10*, 928. [CrossRef]
10. Zhou, Y.; Wang, J.; Fang, Y. Green and High Effective Scale Inhibitor Based on Ring-Opening Graft Modification of Polyaspartic Acid. *Catalysts* **2021**, *11*, 802. [CrossRef]
11. Cheng, Z.; Qin, Q.; Jia, H.; Li, J.; Yan, F.; Meng, X.; Wang, J. Scale evaluation and antiscalant testing based on fluorescent probe technology in RO process. *J. Membr. Sci.* **2021**, *636*, 119598. [CrossRef]
12. Hoang, T.A. Mechanisms of Scale Formation and Inhibition. In *Mineral Scales and Deposits, Scientific and Technological Approaches*, 1st ed.; Amjad, Z., Demadis, K., Eds.; Elsevier: Amsterdam, The Netherlands, 2015; pp. 47–83. [CrossRef]
13. Oshchepkov, M.; Golovesov, V.; Ryabova, A.; Tkachenko, S.; Redchuk, A.; Rönkkömäki, H.; Rudakova, G.; Pervov, A.; Popov, K. Visualization of a novel fluorescent-tagged bisphosphonate behavior during reverse osmosis desalination of water with high sulfate content. *Sep. Purif. Technol.* **2021**, *255*, 117382. [CrossRef]
14. Oshchepkov, M.; Golovesov, V.; Ryabova, A.; Redchuk, A.; Tkachenko, S.; Pervov, A.; Popov, K. Gypsum crystallization during reverse osmosis desalination of water with high sulfate content in presence of a novel fluorescent-tagged polyacrylate. *Crystals* **2020**, *10*, 309. [CrossRef]

15. Popov, K.; Oshchepkov, M.; Kamagurov, S.; Tkachenko, S.; Dikareva, Y.; Rudakova, G. Synthesis and properties of novel fluorescent-tagged polyacrylate-based scale inhibitors. *J. Appl. Polym. Sci.* **2017**, *134*, 45017. [CrossRef]
16. Oshchepkov, M.; Kamagurov, S.; Tkachenko, S.; Ryabova, A.; Popov, K. An Insight into the Mechanisms of the Scale Inhibition. A Case Study of a Novel Task-specific Fluorescent-tagged Scale Inhibitor Location on Gypsum Crystals. *ChemNanoMat* **2019**, *5*, 586–592. [CrossRef]
17. Gal, J.-Y.; Bollinger, J.-C.; Tolosa, H.; Gache, N. Calcium carbonate solubility: A reappraisal of scale formation and inhibition. *Talanta* **1996**, *43*, 1497–1509. [CrossRef]
18. De Visscher, A.; Vanderdeelen, J. IUPAC-NIST Solubility Data Series. 95. Alkaline Earth Carbonates in Aqueous Systems. Part 2. Ca. *J. Phys. Chem. Ref. Data* **2012**, *41*, 023105. [CrossRef]
19. Powell, K.J.; Brown, P.L.; Byrne, R.H.; Gajda, T.; Hefter, G.; Leuz, A.-K.; Sjöberg, S.; Wanner, H. Chemical speciation of environmentally significant metals with inorganic ligands. Part 3: The Pb^{2+} + OH^- , Cl^- , CO_3^{2-} , SO_4^{2-} , and PO_4^{3-} systems (IUPAC Technical Report). *Pure Appl. Chem.* **2009**, *81*, 2425–2476. [CrossRef]
20. Le Guyader, M.; Dorange, G.; Marchand, A.; Hanoun, H. Solubility of calcite and stability constants of complex ions. I. Case of waters that are pure with respect to carbon. *Bull. Soc. Chim. Fr.* **1983**, *9–10*, 203–209.
21. SPECIES. Academic Software. In *Solution Equilibria: Principles and applications (for Windows 95, 98 and NT); Release 1*; Powell, K.J. (Ed.) Academic Software: London, UK, 2004.
22. Popov, K.; Rudakova, G.; Larchenko, V.; Tusheva, M.; Afanas'eva, E.; Kombarova, S.; Kamagurov, S.; Kovaleva, N. A comparative performance ranking of some phosphonates and environmentally friendly polymers on CaCO_3 scaling inhibition by NACE protocol. *Des. Water Treatm.* **2017**, *69*, 163–172. [CrossRef]
23. Liu, Y.; Zhou, Y.; Yao, Q.; Huang, J.; Liu, G.; Wang, H.; Cao, K.; Chen, Y.; Bu, Y.; Wu, W.; et al. Double-hydrophilic polyether antiscalant used as a crystal growth modifier of calcium scales in cooling-water systems. *J. Appl. Polym. Sci.* **2014**, *131*, 39792. [CrossRef]
24. Demadis, K.D.; Yang, B.; Young, P.R.; Kouznetsov, D.L.; Kelley, D.G. Rational Development of New Cooling Water Chemical Treatment Programs for Scale and Microbial Control. In *Advances in Crystal Growth Inhibition Technologies*; Amjad, Z., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2002; pp. 215–234. [CrossRef]
25. Popov, K.; Oshchepkov, M.; Kovalenko, A.; Redchuk, A.; Dikareva, J.; Pochitalkina, I. Scale nucleation natural precursors: A case study of “micro/nanodust” impurities nature in laboratory aqueous samples obtained from Moscow tap water. *Int. J. Corros. Scale Inhib.* **2020**, *9*, 1097–1112. [CrossRef]
26. Oshchepkov, M.; Popov, K.; Kovalenko, A.; Redchuk, A.; Dikareva, J.; Pochitalkina, I. Initial stages of gypsum nucleation: The role of “nano/microdust”. *Minerals* **2020**, *10*, 1083. [CrossRef]
27. Zhang, Z.; Lu, M.; Liu, J.; Chen, H.; Chen, Q.; Wang, B. Fluorescent-tagged hyper-branched polyester for inhibition of CaSO_4 scale and the scale inhibition mechanism. *Materials Today Comm.* **2020**, *25*, 101359. [CrossRef]
28. Popov, K.; Rudakova, G.; Larchenko, V.; Tusheva, M.; Afanas'eva, E.; Kombarova, S.; Kamagurov, S.; Kovaleva, N. Comparative performance evaluation of some novel «green» and traditional antiscalants in calcium sulfate scaling. *Adv. Mat. Sci. Eng.* **2016**, *10*, 17–19. [CrossRef]
29. Ang, H.M.; Muryanto, S.; Hoang, T. Gypsum scale formation control in pipe flow systems: A systematic study on the effects of process parameters and additives. In *Gypsum: Properties, Production and Applications*; Sampson, D.H., Ed.; Nova Science Publishers: New York, NY, USA, 2011; pp. 1–33.
30. Sheng, K.; Ge, H.; Huang, X.; Zhang, Y.; Song, Y.; Ge, F.; Zhao, Y.; Meng, X. Formation and inhibition of calcium carbonate crystals under cathodic polarization conditions. *Crystals* **2020**, *10*, 275. [CrossRef]
31. Tkachenko, S.; Ryabova, A.; Oshchepkov, M.; Popov, K. Fluorescent-tagged Antiscalants: A New Look at the Scale Inhibition Mechanism and Antiscalant Selection. *ChemNanoMat* **2022**, *8*, 2, in press. [CrossRef]



Article

Comparison of Artificial Intelligence Control Strategies for a Peristaltically Pumped Low-Pressure Driven Membrane Process

José-Luis Díez ^{1,2}, Vicente Masip-Moret ³, Asunción Santafé-Moros ⁴ and José M. Gozávez-Zafrilla ^{4,*}

¹ Instituto Universitario de Automática e Informática Industrial, Universitat Politècnica de València, 46022 València, Spain

² Centro de Investigación Biomédica en Red de Diabetes y Enfermedades Metabólicas Asociadas (CIBERDEM), Instituto de Salud Carlos III, 28029 Madrid, Spain

³ Barcelona Supercomputing Center, 08034 Barcelona, Spain

⁴ Institute for Industrial, Radiophysical and Environmental Safety (ISIRYM), Universitat Politècnica de València, 46022 València, Spain

* Correspondence: jmgz@iqn.upv.es; Tel.: +34-963877633

Abstract: Peristaltic pumping is used in membrane applications where high and sterile sealing is required. However, control is difficult due to the pulsating pump characteristics and the time-varying properties of the system. In this work, three artificial intelligence control strategies (artificial neural networks (ANN), fuzzy logic expert systems, and fuzzy-integrated local models) were used to regulate transmembrane pressure and crossflow velocity in a microfiltration system under high fouling conditions. A pilot plant was used to obtain the necessary data to identify the AI models and to test the controllers. Humic acid was employed as a foulant, and cleaning-in-place with NaOH was used to restore the membrane state. Several starting operating points were studied and setpoint changes were performed to study the plant dynamics under different control strategies. The results showed that the control approaches were able to control the membrane system, but significant differences in the dynamics were observed. The ANN control was able to achieve the specifications but showed poor dynamics. Expert control was fast but showed problems in different working areas. Local models required less data than ANN, achieving high accuracy and robustness. Therefore, the technique to be used will depend on the available information and the application dynamics requirements.

Keywords: low-pressure driven process; peristaltic pump; microfiltration; intelligent control; artificial intelligence; modelling; fouling; humic acid

1. Introduction

Peristaltic pumping is used in membrane processes, such as microfiltration (MF) or ultrafiltration (UF), when high sealing without contact of the solutions with the lubricating fluids or friction elements is required. Typical applications of this configuration are in food processing industry separations, membrane bioreactors, membrane medical applications, and laboratory experimentation.

The use of peristaltic pumps in membrane bioreactor systems also has the advantage of diminishing the effect of tearing stress. For example, anaerobic sludge membrane reactors using peristaltic pumping for pressure application and recirculation have been used to treat municipal or industrial waters [1,2]. This kind of pumping allows special membrane applications such as the use of fluidized glass beads to improve membrane performance [3].

In medical systems using membranes, mainly in artificial kidneys or microdialysis sensors, pumps must not introduce harmful agents and must maintain sterility. Peristaltic pumps can meet this requirement with suitable flow rate characteristics [4]. However, problems related to the formation of particles may occur. These particles may be caused by wear of the tube due to spallation [5] or degradation of the solution. An example of the

latter situation is the formation of protein particles caused by the effect of the tube tearing on proteins adsorbed on the tube walls [6].

The combination of peristaltic pumps and membranes is also widely used on a laboratory scale. For example, multi-channel peristaltic pumps can perform many membrane experiments at the same time [7] or experiments in which two peristaltic pumps work in opposite directions [8].

1.1. Modelling of Peristaltically Pumped Low-Pressure Driven Membrane Systems

The development of control systems to meet permeate flow specifications is essential for the proper functioning of the above-mentioned applications.

Most control systems are, in some way, model based. Therefore, the existence of a computational model deduced from the physical behavior of the system can facilitate control development. However, modeling and control of peristaltically pumped MF or UF membrane systems can be more challenging than other membrane configurations.

The behavior and performance of peristaltic pumps can be approximately modeled by lumped models based on physical considerations [9] or by using computational fluid dynamics [10]. Disturbance models can also be used for control purposes [11]. However, let us suppose that more accurate time-varying models are needed for control. In that case, the models could be improved by taking into account changes in feed properties and mechanical characteristics of the tubing material.

Membrane modelling must describe the permeate flux and component rejection and its evolution over time. In MF, retention depends on particle size and pore size distribution. The flow through the pores can be described by Poiseuille's law. In UF, modelling of solute and solvent transport is based on hydrodynamic equations describing hindered diffusion and convection [12]. For most processes, fouling adds additional resistance to flow. Moreover, the effect of fouling involves longer time dynamics than those caused by feed or operational variations. To describe the different fouling mechanisms (pore blocking or gel layer formation), empirical models such as those developed by Hermia can be used [13]. Other modelling difficulties are the different fouling potential of the solutions [14], the important effect of spacer design on fouling [15], and the fact that the membrane performance does not fully recover after the cleaning procedures. For both processes (MF and UF), the situation can be more complex in the case of a non-constant flow [16], as in the case of the pulsating flow produced by a peristaltic pump.

1.2. Intelligent Control Approaches for Low-Pressure Membrane Systems

In conclusion, accurate modeling of peristaltically pumped low-pressure driven membrane systems is challenging due to the changes in system performance over time. In general, models derived from first principles with sufficient accuracy are very complex. Therefore, classical control techniques cannot be applied directly. On the other hand, those models simple enough to apply well-known control techniques cannot describe the long-term behavior of the system. This fact led the authors to consider the use of artificial intelligence (AI) and system identification methods as the most appropriate approach.

Most attempts to control peristaltically pumped membrane systems have come from the field of hemodialysis, where accurate control of fluid delivery is especially critical [17,18]. In this application, the use of hierarchical adaptive and supervisory control has allowed adjusting the pump inputs to patient monitoring data [19].

In other fields where MF or UF have been applied, the modeling and control focus on the interaction of the membrane and the pump, but on the membrane performance. Niu et al. have recently carried out a critical review on the use of different AI methods in fouling prediction [20]. They found that the most modeled features were transmembrane pressure, flux dynamics, and flux decline by fouling. They divided the AI techniques into single and hybrid algorithms. They indicated that the most employed single algorithm was artificial neural networks (ANN), but others such as fuzzy logic, genetic programming, or support vector machines were also used. Hybrid algorithms were usually built by

combining these techniques with a search algorithm. Jawad et al. conducted a review that found that permeate flux is the most modeled feature in the different MF or UF applications. The same study showed that the most used model input is transmembrane pressure (TMP), and that the composition-related parameters were also used as input in the different works [21]. Recently, machine learning has been used to model the dynamics of filtration and backwashing of UF by a back propagation ANN [22]. Ultrafiltration of protein solutions has been effectively modeled using ANN for a tubular crossflow membrane [23]. This work used as inputs: operational time, pH, and ionic strength; and as outputs: filtrate flow and protein transmission. The authors compared the performance of ANN with that of the Hermia models [24] and obtained similar performance results for the fitted experiments, but better ANN extrapolation capability for experiments not included in the fitting process. Other AI-based modelling tools, such as fuzzy logic, have proven to be an alternative to ANN modelling [25].

1.3. Selection of Study Case for Comparison of Control Approaches

Given the promising results found in the literature on AI methods applied to low-pressure driven processes, this work aimed to compare the performance of a set of AI modeling techniques for controlling peristaltically pumped membrane processes subjected to strong fouling. The specific process case studied used a ceramic MF membrane with a pore size close to the maximum UF pore size range. The operating conditions of the MF system to be controlled were average crossflow velocity and average transmembrane pressure. Forced membrane fouling was expected to produce permeability variability due to both reversible and irreversible fouling.

The chosen techniques cannot only provide an accurate system description but can also deliver models that are good for subsequent control design under all the expected operating conditions. This balance between modeling and control could lead to a better performance of the controlled MF system. Therefore, a comparison between the available methods was made to determine which can be more effective in controlling the operating conditions in a changing membrane system.

In order to obtain the data necessary for the creation of the models, each experiment consisted of an operational step with fouling followed by a cleaning step. For the first step, the selected foulant was humic acid at a relatively high concentration. Humic acid fouling is one of the main factors limiting MF in water treatment [26,27] with humic acid aggregates being responsible for most of the fouling [28]. For the second step, it was considered that fouling by organic matter can be removed from ceramic membranes by cleaning-in-place (CIP) procedures using alkalis. When NaOH is used, typical concentrations are in the range of 0.5–2% wt. [29,30]. The combination of rapid fouling with humic acid and subsequent cleaning with NaOH allowed short dynamic experiments with a rapid decrease in flow rate suitable for model identification and control design.

The structure of this article is as follows. Section 2 explains the system developed for the experiments, the experimental methods, and the model identification and control procedures. Section 3 shows the results obtained for the three strategies considered: ANN, fuzzy logic, and local models. Section 4 discusses the differences between the control strategies studied. Finally, the Conclusions section summarizes the results and proposes ways forward for further study.

2. Materials and Methods

2.1. Experimental Setup

Figure 1 shows a schematic of the pilot plant used in the experiments. The feed tank of the main circuit had a volume of 28 L and was tempered in a Polyscience recirculating unit. The main circuit contained a Micro CARBOSEP/Kerapac laboratory module. The peristaltic pump used was the Masterflex I/P® brushless process drive with high-performance pump head able to work from 33 to 650 rpm. The tubing used was Norprene HP 06404-70 with an internal diameter of 9 mm. Downstream of the pump, a pulse damper was placed,

constructed from a helical rubber tube. Two Bürket 8323 pressure sensors prepared to work in the 0–4 bar range were placed in the inlet and outlet of the membrane module. A Bürket 8031 flow sensor with a range of 10 to 100 L/h was placed at the membrane outlet to measure the crossflow during fouling experiments and CIP operations. For permeate flow measurement, a device for low flow rates was built ad-hoc. The flow measurement was based on alternate filling and emptying of a permeate collection tank controlled by a solenoid valve and measurement of the position of a buoy with a laser sensor. Two three-way solenoid valves controlled the alternation between a fouling operation step, an alkali cleaning step, and water flushing between both stages. Pump control and acquisition of flow rate and pressure data were performed using a PCB circuit. An Advantech PC1-1711 DAQ card installed in a PC was used to record sensor data and send control actions to the actuators (valves and pump). The user interface was performed in Matlab.

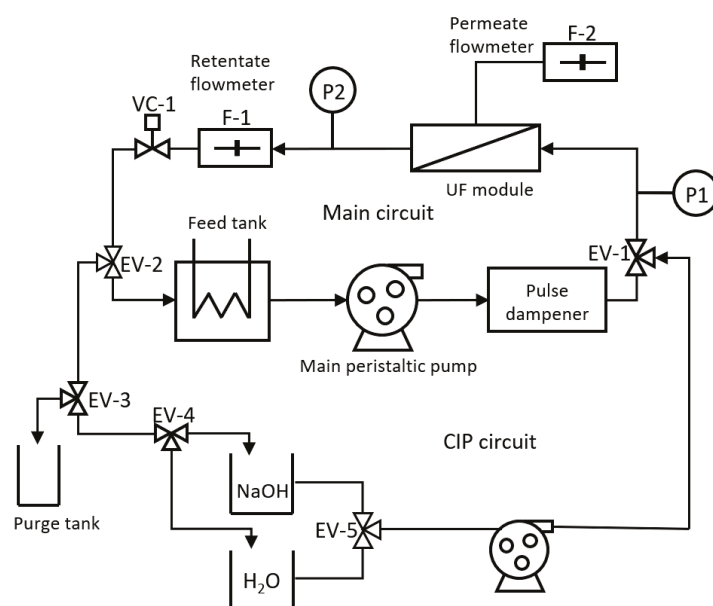


Figure 1. Schematic of the pilot plant.

The membrane used in the experiments was the Carbosep M14. This membrane is a tubular ceramic membrane with a length of 400 mm and membrane area of 75.4 cm², a nominal cut-off threshold of 0.14 µm, and a nominal water flow rate of 375 L·h^{−1}·m^{−2}·bar^{−1}.

2.2. Experimental Conditions

Model identification experiments were performed using humic acid sodium salt (technical grade from Sigma-Aldrich) at a concentration of 20 mg/L. This concentration was high enough to produce severe fouling in a short time. The experiments were carried out between 2 and 5 h. The temperature of the feed tank was maintained at 25 °C. The applied pressure range to build the model was between 0.3 to 2.5 bar. During the experiments, the inlet and outlet pressure, the concentrate flow rate, and the permeate flow were sampled at a rate of 1 s. The solenoid valve opening percentage and pump rotational speed were the two variables manipulated by the control system during the fouling operating stage to meet the pressure and flow requirements. The control actions were carried out at a rate of 20 s. To recover the permeate flow, a CIP operation was performed after each model identification experiment using a 0.1 mol/L sodium hydroxide solution.

2.3. Control Strategies

Three different approaches were used to control the system, requiring different strategies to incorporate the information available from the systems and build the controllers:

(i) artificial neural networks, (ii) expert control based on fuzzy logic, and (iii) control by fuzzy-integrated inverse local models.

2.3.1. Control Based on Artificial Neural Networks (ANN)

An artificial neuron is an element that has an internal state (activation level) that receives signals that can change its state. An artificial neural network (ANN) is a structure capable of processing information defined as input variables to obtain a response expressed as output variables. The ANN is organized in layers of neurons in which their parameters (weights w_i and biases b_i) must be determined to match the mapping between inputs and outputs. The fitting procedure to obtain the ANN parameters is known as training. In this case, a non-supervised learning strategy has been used in which the data is divided into one dataset for training, one for validation, and one for testing. Given an experimental output obtained for the input conditions, the errors between the experimental output vector and the response predicted by the ANN in its current state of adjustment against the input are evaluated. The error obtained is used to adjust the values of the weights and biases. The validation data set is used to measure the overall error of the network and determine when to stop training the ANN. In our case, a layer of neurons with linear output and radial activation functions (Figure 2) gave satisfactory results.

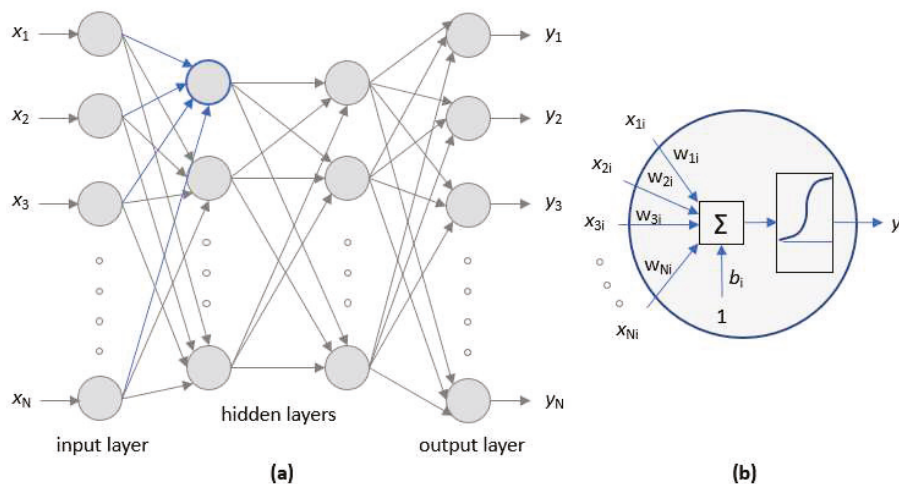


Figure 2. Artificial neural network: (a) layers structure, (b) detail of a neuron.

The model identified by ANN can be used to predict the behavior of the system, but in this case, the objective was to control the system. Therefore, an ANN-based control technique is needed. The designed controller was based on one of the simplest control ideas that are applicable when a model of the system to be controlled is available: given a desired reference to be followed by a system, the reference passed through the inverse model gives the control action to be injected to the system to achieve the desired reference. In real-world applications, subjected to disturbances, this simple structure is complemented with additional elements. In this case, a classic direct control with reverse pre-feed (see Figure 3) based on two ANN and a reference model is used [31]. The ANN is used twice in this case. In the first step, the error, defined as the difference between the real (Y_{comp}) and the desired (ref) output of the system is fed into a predefined reference model (the desired behavior of the plant) giving an output (reff). This output goes to the inverse of the ANN system model, providing then a control action (U_n) which is compared to the control action (U_{PI}) given by a proportional-integral controller (PI) designed for the reference model. This comparison generates the final control action (U) to be fed into the real system. This control action is also fed into the ANN system model, whose output is compared to the real output and the difference feeds back to the reference. Next, the reference is compensated with the difference between the real output of the plant and the output predicted by a non-affine ANN and this error initiates the control actions computation again.

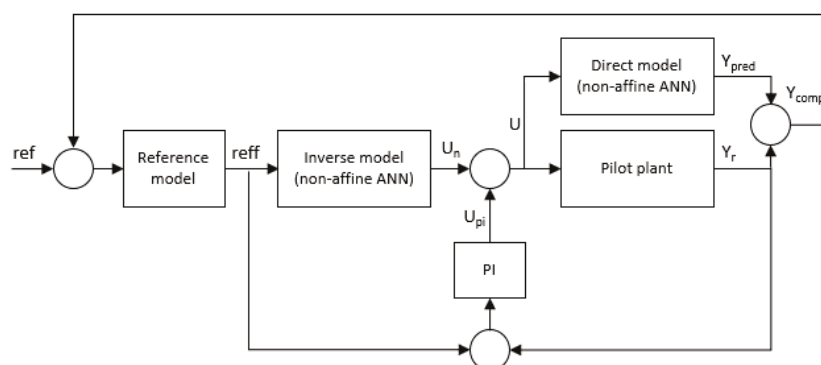


Figure 3. Direct control with reverse pre-feed based on artificial neural networks.

Therefore, the identification procedure required the identification of two ANNs. First the direct model, which provides the output prediction, was identified. The inputs used to train the ANN were the output in the previous time and the inputs for the plant operation (solenoid valve opening rate and pump rotation speed). Secondly, the inverse model was identified after applying low-pass filtering to the signal. The Neural Network toolbox of Matlab was used for both identifications.

The experimental data were obtained in the working area of the plant for a matrix of combinations of pump speed signals in the range of 0.5–3 V (108–650 rpm) and valve opening in the range of 65% to 80%.

2.3.2. Expert Control Based on Fuzzy Logic

The term fuzzy logic was introduced in 1965 with the Lotfi Zadeh's proposal of fuzzy set theory [32]. In contrast with Boolean logic which only considers false/truth values of variables expressed by the integers 0 or 1, in fuzzy logic, the level of truth of a variable can be expressed by any real number between 0 and 1. This is a natural way of representing vagueness and imprecise information and has been applied to many fields.

From a practical view, a fuzzy system can be seen as a linguistically interpretable model consisting of several "if-then" rules and logical operators using fuzzy sets as input and output variables:

$$\text{If input is } A \text{ then output is } B \quad (1)$$

A rule-based fuzzy system, although it is a mathematical function and can be identified from data similar to any other system, can make direct use of expert information as long as it is interpretable. Therefore, experts in the operation of a specific system can easily build a model or a controller without any modelling or control knowledge.

In this case, a fuzzy controller was built for the MF system defined above, based on the available knowledge of the experts. The expert (in close collaboration with the control engineer) defined the linguistic variables and the fuzzy rules. The Matlab Fuzzy Systems toolbox was used for implementation purposes.

Although two independent fuzzy controllers can be built to control TMP and retentate flow rate separately, it was thought that a multivariable controller could give better results by taking into account their interaction. Combining expert information and control possibilities, the structure presented in Figure 4 was agreed upon, aiming for fast and accurate control. The main ideas were to quickly drive the system close to the desired TMP/flow operating point, and then fine-tune the control around this point more precisely but more slowly.

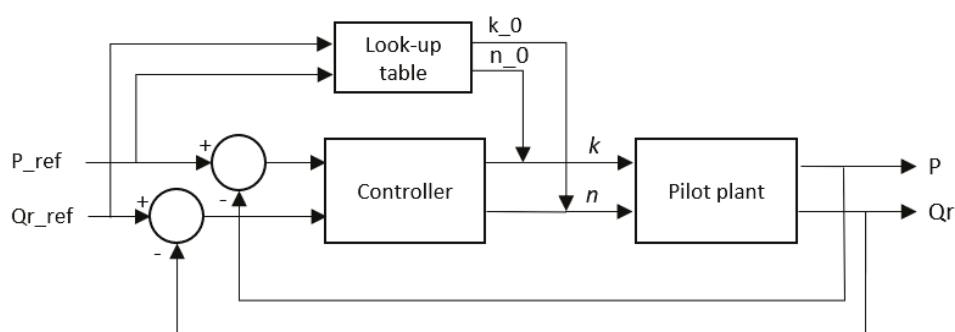


Figure 4. Diagram of the fuzzy controller.

The first fast part can be accomplished using a look-up-table (LUT) strategy [33]. The inputs of this table are the desired TMP (P_{ref}) and the retentate flow rate (Q_{r_ref}) at the operating point, and its outputs are the valve opening percentage (k_0) and the pump speed (n_0) control actions to reach approximately the reference under standard base conditions.

These base control actions can be modified to new values (k and n) by a fuzzy controller whose input variables are the transmembrane pressure error and the retentate flow error, thus closing the gap between the actual output results (P and Q_r) and the desired ones (P_{ref} and Q_{r_ref}).

2.3.3. Control by Inverse Local Models

By making use of the expert system information on the operating points defined in the LUT (or any other partition of the input space) defined in the previous section, a more classical control approach can be used. The idea is the opposite of the ANN approach where a very accurate model of the systems is obtained to perform a good control of the plant based on a complex controller. In this case, very simple models of the system must be identified at each of the required operating points and a simple controller must be designed for each of the models. Subsequently, all available control actions are integrated into a single control action depending on the actual operating point. The complete controller can be built, for example, as a fuzzy system [34] in which each controller at each operating point is a rule, and the outputs are interpolated using membership functions created by weighting the distances to the operating points (Figure 5).

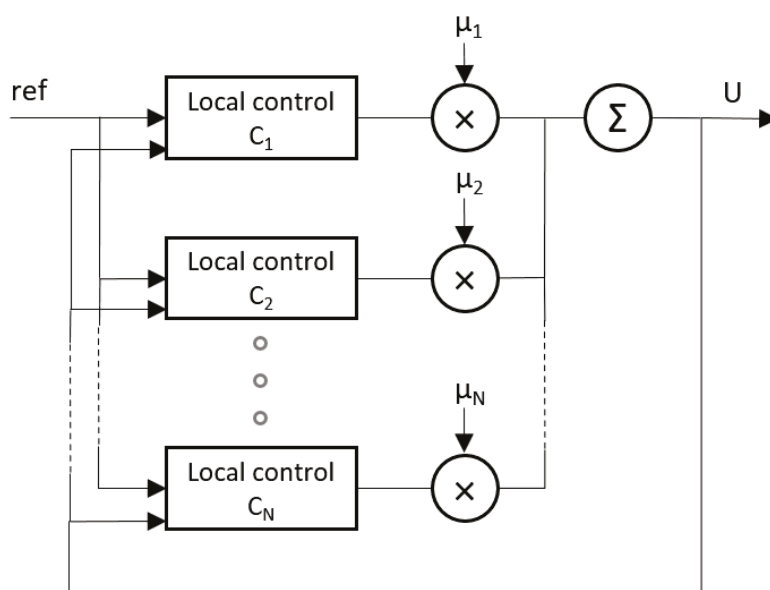


Figure 5. Control structure with local models.

Therefore, the idea was to identify several models for relating inputs vs. outputs of the system (i.e., Vel and %Ev vs. P_ref and Qr_ref in the previous section) that contain only the gain information between each pair of variables at each operating point. The information included in each pair-of-variables local model can be arranged into a matrix where the increments of each output with respect to each input associated with an operating point can be easily organized:

$$\begin{bmatrix} \Delta P \\ \Delta Q \end{bmatrix} = \begin{bmatrix} \left. \frac{\partial P}{\partial n} \right|_{ko} & \left. \frac{\partial P}{\partial k} \right|_{no} \\ \left. \frac{\partial Q}{\partial n} \right|_{ko} & \left. \frac{\partial Q}{\partial k} \right|_{no} \end{bmatrix} \cdot \begin{bmatrix} \Delta n \\ \Delta k \end{bmatrix} \quad (2)$$

where, for the sake of clarity, n is pump speed Vel, k is solenoid valve opening %Ev, P is transmembrane pressure TMP, and Q is flow rate Qr. In this framework, the derivatives of the local function directly relate the required control actions and the desired change in operating conditions for a particular operating point (ko, no) .

The controller for both outputs at the same time was easily obtained by inverting the derivative matrix:

$$\begin{bmatrix} \Delta n \\ \Delta k \end{bmatrix} = \begin{bmatrix} \left. \frac{\partial P}{\partial n} \right|_{ko} & \left. \frac{\partial P}{\partial k} \right|_{no} \\ \left. \frac{\partial Q}{\partial n} \right|_{ko} & \left. \frac{\partial Q}{\partial k} \right|_{no} \end{bmatrix}^{-1} \cdot \begin{bmatrix} \Delta P \\ \Delta Q \end{bmatrix} \quad (3)$$

However, although the simple gain models in each cell of the matrix can easily be inverted (thus having an inverse system model at each operating point for a particular input-output combination), the two-inputs–two-outputs derivative matrix in Equation (2) is not always invertible (values close to zero, or one row/column is linearly dependent on another).

If it is the case and the system is not very fast (as in MF), an approximate multivariable control can be achieved by alternating small steps of single input-output control actions for each of the matrix cells in Equation (3). Figure 6 shows the final control diagram used in the control of the process, where a “control strategy” defines the alternate operation of the single-input–single-output controllers based on the inverse of the appropriate matrix cell.

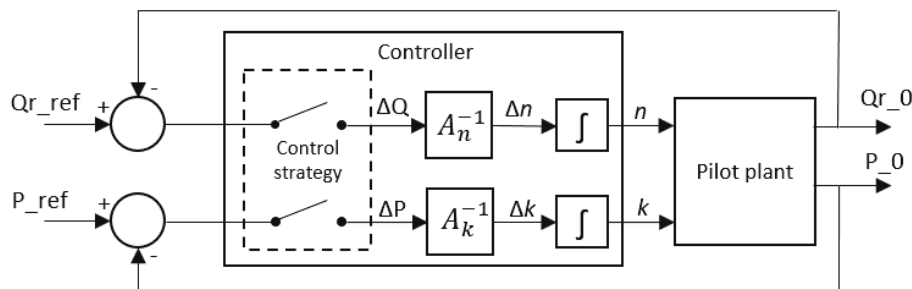


Figure 6. Global control diagram in an operating point.

Recall that there is a controller, as defined in Figure 6, for each predefined operating point j in the (n, k) plane, and all of them are integrated using the scheme showed in Figure 5. The integration is performed by weighting each control action j by its membership function μ_j calculated as the relative distance from the actual operating point of the plant to the local operating point j of the model/controller. Whenever our system operates in the (n, k) plane of operating points, a particular operating point (n_i, k_i) of the plant at instant i will be surrounded by 4 operating points, and the normalized membership (from 0 to 1) of, e.g., the operating point i (out of 4) can be calculated as [35]:

$$\mu_i = \frac{\frac{1}{d_i}}{\sum_{j=1}^4 \frac{1}{d_j}} \quad (4)$$

where d is the absolute value of the Euclidean distance from the actual operating point of the plant to the 4 nearest predefined operating points in the controller.

3. Results and Discussion

3.1. Control Based on Artificial Neural Networks

The neural network structure used to build the direct and inverse ANN models of the controller had two hidden layers with 6 neurons per layer. The non-affine ANN used as inverse models had an input layer with 8 neurons. This structure permitted a reasonable balance between training time and prediction capability. The best training results were obtained using the Levenberg-Marquardt algorithm. Model identification results were reasonably good for both the direct and inverse models at most operating points.

The controller was tested on a 7×7 matrix of equally spaced operating setpoints given by combinations in pump speed signal ranging 0.5–3 V (108–650 rpm) and valve opening percentages from 65% to 80%. Figure 7 shows the trajectories in the flow-pressure space of the controlled pilot plant. The ANN-based control was able to achieve the desired reference (static specifications). However, these satisfactory results could be improved from the dynamic specifications point of view since the controlled system showed significant overshoot and long settling time during the plant start-up at some operating points (Figure 8). This behavior was a consequence of a poor identification of the process dynamics when the network was trained using the entire dataset.

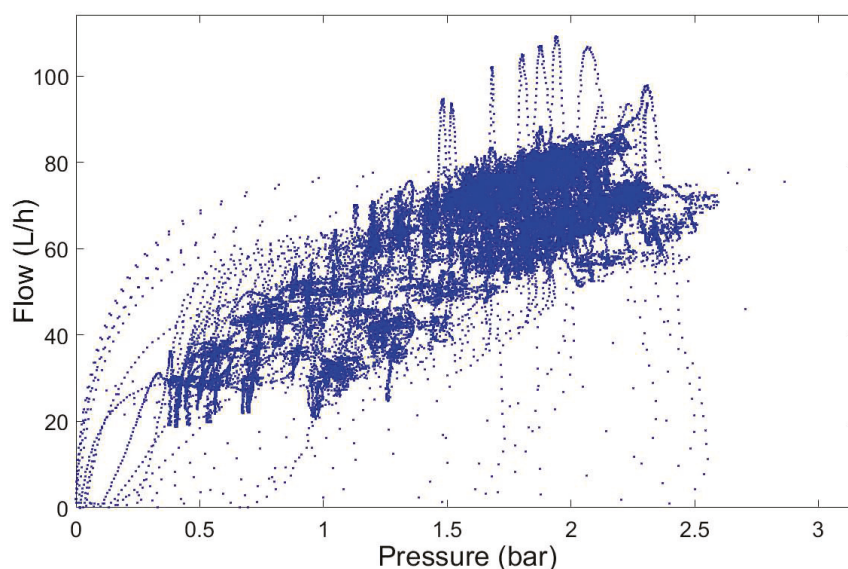


Figure 7. Operating working area of the pilot plant obtained for pump signal speed 0.5–3 V (108–650 rpm) and valve opening 65–80%.

3.2. Expert Control Based on Fuzzy Logic

In order to represent the expert knowledge on plant operation in a Mamdani rule-based expert system with a number of fuzzy rules as in Equation (1), the “vocabulary” of fuzzy input and output variables was first defined.

The input variables to the fuzzy controller in Figure 4 were the transmembrane pressure error (eP) and the retentate flow rate error (eQ). First, the ranges of values of the inputs were established to obtain the membership functions. The pressure error was divided into the following categories: very negative (VN), negative (N), slightly negative (NS), zero (Z), slightly positive (PS), positive (P), and very positive (VP). The same categories were used to divide the flow rate range. The above definitions, in combination with the information provided by experts, were translated into the fuzzification structure presented in Figure 9.

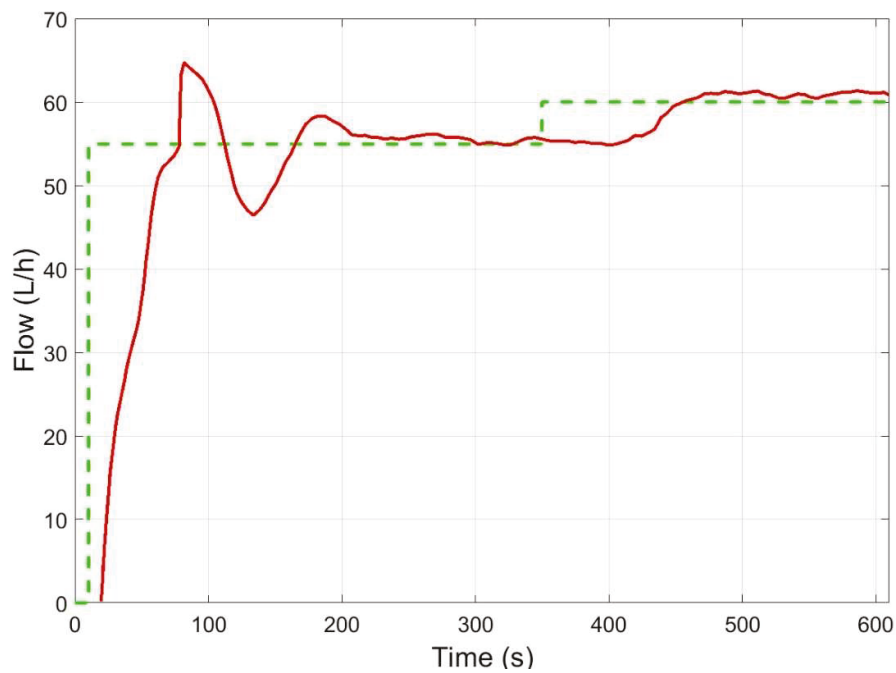


Figure 8. Control dynamics of ANN controller (flow rate reference in dashed green and flow output in red).

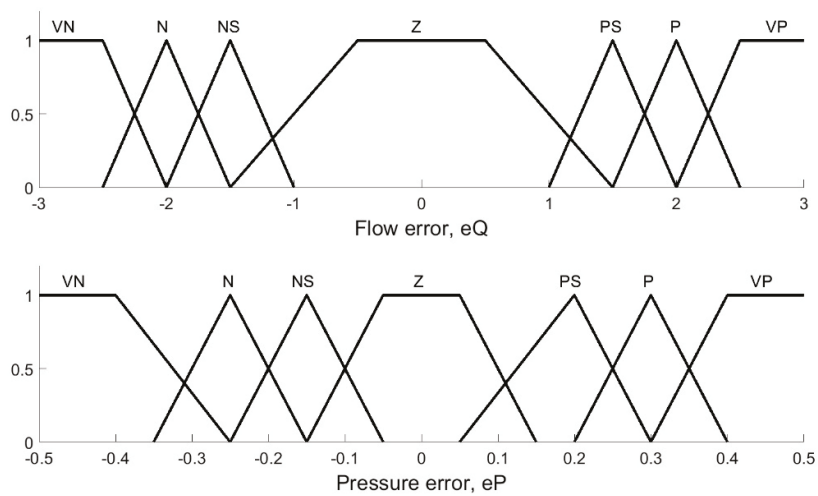


Figure 9. Linguistic values assigned to the controller inputs.

Linguistic values were also assigned to the controller outputs in Figure 4: pump speed and valve opening. All the linguistic variables are shown in Table 1, and the resulting defuzzification structure is shown in Figure 10.

Table 1. Linguistic variables of the controller output.

	Pump Speed	Valve Opening
increase (high)	NIH	KIH
increase (medium)	NIM	KIM
increase (slight)	NIS	KIS
decrease (slight)	NDS	KDS
decrease (medium)	NDM	KDM
decrease (high)	NDH	KDH

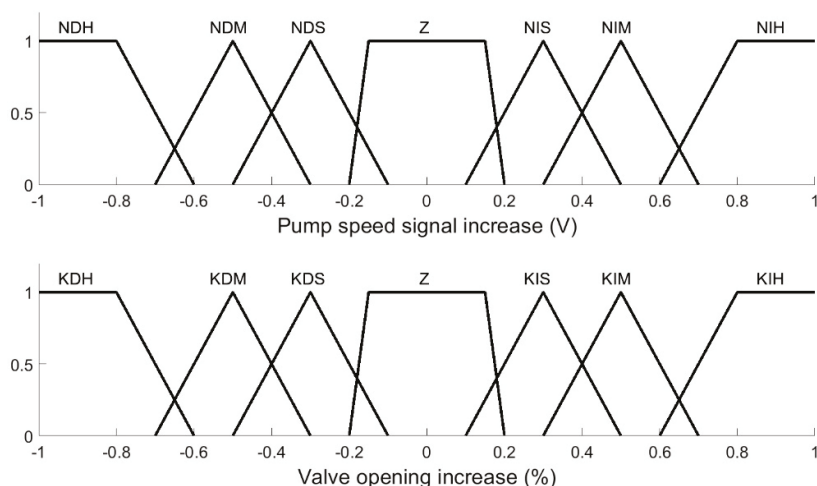


Figure 10. Linguistic values assigned to the controller outputs.

Once all the linguistic variables and their ranges were defined, the expert in the operation plant was able to translate all his/her knowledge using the limited vocabulary in the expert rules in Table 2. Each row is a possible eQ input, and each column is one of the eP input possibilities. Each cell in the table represents the outputs to be applied. For example, the first cell of the table corresponds to the rule:

$$\text{If } eQ \text{ is } VN \text{ and } eP \text{ is } VN \text{ then pump speed is } NDH \quad (5)$$

Next, a fuzzy rule-based system composed of 49 rules as described above was then defined to perform the control of the MF plant.

Table 2. Expert rules for the fuzzy controller according to defined fuzzy variables for inputs and outputs.

eQ/eP	VN	N	NS	Z	PS	P	VP
VN	NDH	KDM NDM	NDM	KDM NDS	NIS	KDM	KDM NIM
N	NDH	NDM	NDM	KDM	KDS NIS	KDM	KDM NIS
NS	NDM	NDM	NDS	KDS	KIS	KIM	NIM
Z	KIS	NDM	KIS	-	KDS	NIM	NIM KDS
PS	KIM	KIM	KIS	KIS	KDS NIS	NIM	NIM
P	KIH	KIM	KIM	KIM	NIM	NIM	NIM
VP	KIH	KIS NDS	KIS	KIS NIS	KDS	KDS	NIH

The combination of all the information provided by the expert (linguistic variables and rules) resulted in the nonlinear response surface of the controller for both outputs. The controller performance can be seen for different operating points in Figure 11, with lower overshoot and settling time than in the ANN approach for the same operating conditions.

The performance of the controller was also good for long experiments (about 4 h), where the effect of fouling changed the plant behavior, as shown in Figure 12. The experiments were repeated several times. The figure shows 3 cycles for pressure and flow control at the operation point (55 L/h, 1.5 bar).

Finally, some experiments were performed to see the behavior of the controller when changing the operating point. The results are shown in Figure 13.

3.3. Control by Fuzzy-Integrated Inverse Local Models

The 49 operating points, defined in the previous section, covering the entire operating space of the plant were also considered in this study. A local model was identified for each of them following Equation (2), and a local controller designed as in Equation (3).

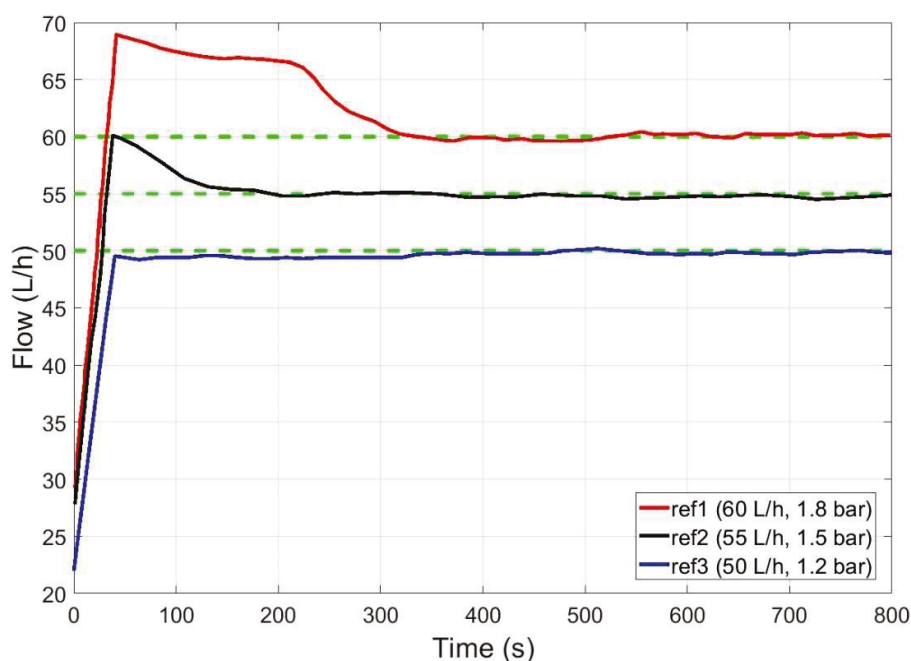


Figure 11. Controller performance for flow rate at different operating points defined by flow rate and pressure (flow references are marked in dashed green in all cases).

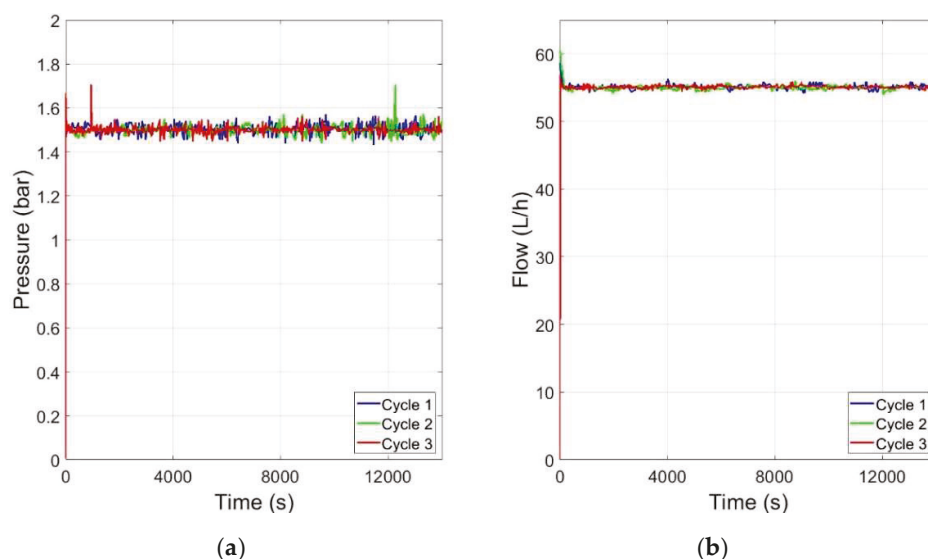


Figure 12. Controller performance in long time runs at the operation point (55 L/h, 1.5 bar): (a) operating point for pressure; (b) operating point for flow rate.

In order to reach a desired operating point (P_{ref} , Q_{r_ref}) while avoiding the inversion problem in Equation (3), the alternate operation of the two controllers shown as “control strategy” in Figure 6 was:

- Reach Q_{r_ref} using the pump speed control variable Vel , but with the solenoid valve fully open (for security reasons)
- If more pressure is needed, then close the solenoid valve by controlling the valve opening $\%Ev$ to reach P_{ref}
- The last action will decrease the flow. Then reach again Q_{r_ref} using the pump speed control variable Vel .
- Follow the last two steps until both references (P_{ref} , Q_{r_ref}) are obtained.

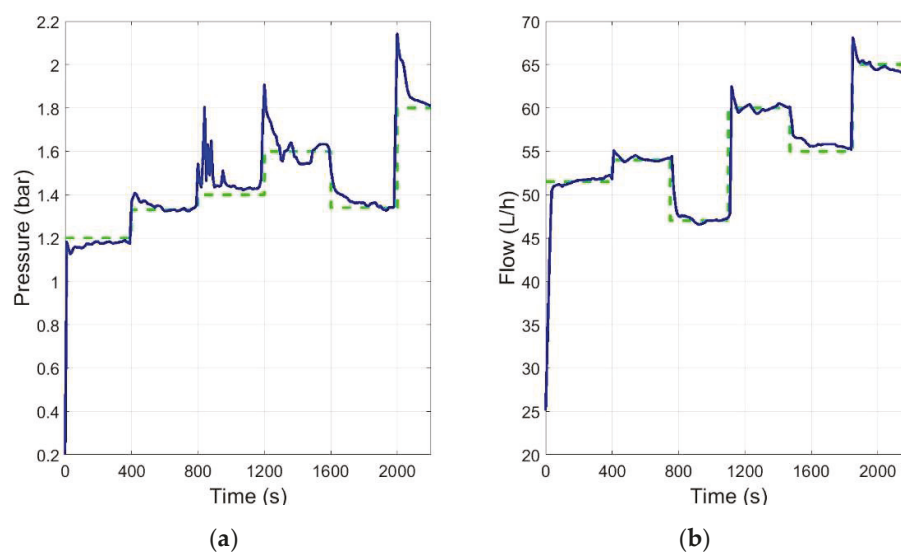


Figure 13. Controller performance (reference in green and output in blue): (a) change of the operating point for pressure; (b) change of operating point for flow.

The desired operating point (P_{ref} , Q_{r_ref}) need not be exactly one of the 49 predefined operating points. Therefore, an interpolation strategy of the control actions was defined (Equation (4)). Figure 14 shows, in the flow-pressure plane, how a representative operating point ($P_{ref} = 2$ bar, $Q_{r_ref} = 54$ L/h) was reached using the proposed strategy.

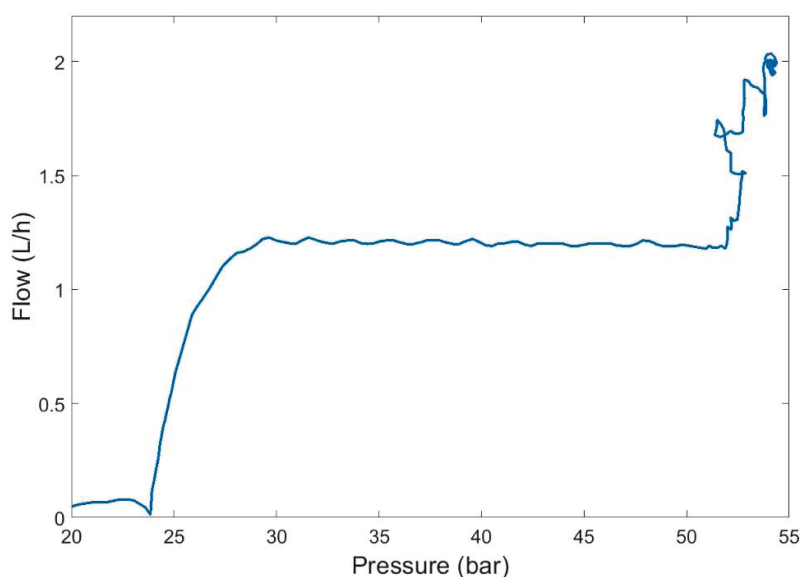


Figure 14. Flow-pressure path followed to reach a predefined operating point ($P_{ref} = 2$ bar, $Q_{r_ref} = 54$ L/h) using the proposed strategy.

Figures 15–18 then show the evolution over time of the outputs and control actions in the same experiment. The results of the new strategy (inverse local models) are plotted in blue, while the best strategy so far (expert control based on fuzzy logic) is plotted in red for ease of comparison.

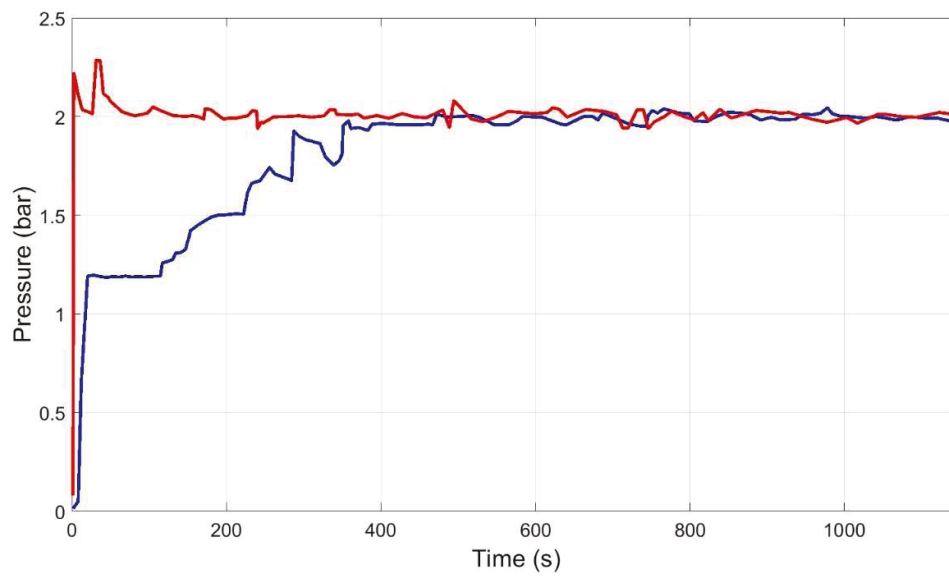


Figure 15. Evolution of pressure output to reach the representative operating point ($P_{ref} = 2$ bar, $Q_{r_ref} = 54$ L/h) using inverse local models (blue), and expert control based on fuzzy logic (red).

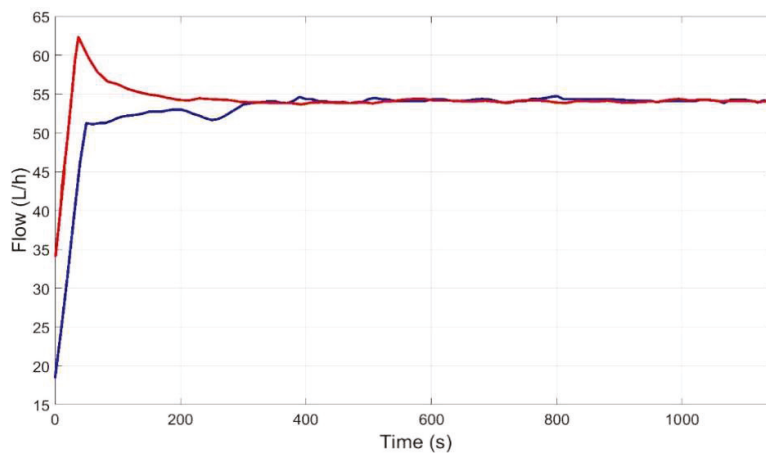


Figure 16. Evolution of flow output to reach the representative operating point ($P_{ref} = 2$ bar, $Q_{r_ref} = 54$ L/h) using inverse local models (blue), and expert control based on fuzzy logic (red).

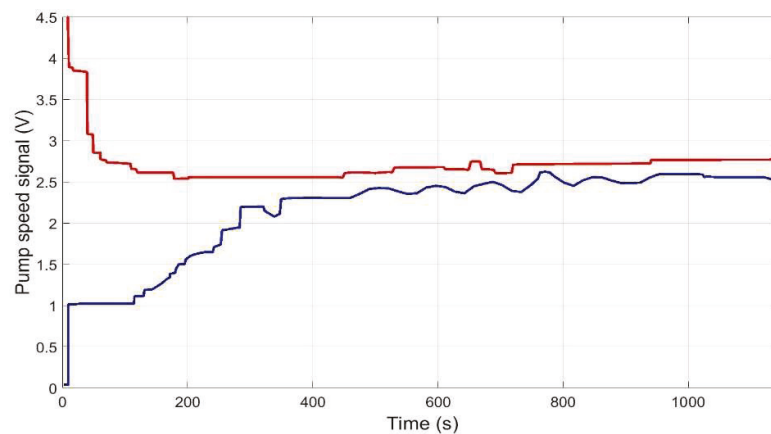


Figure 17. Evolution of pump speed control action to reach the representative operating point ($P_{ref} = 2$ bar, $Q_{r_ref} = 54$ L/h) using inverse local models (blue), and expert control based on fuzzy logic (red).

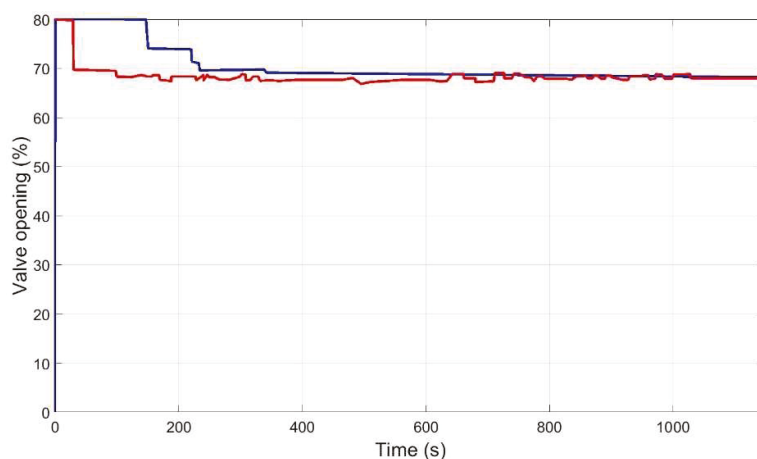


Figure 18. Evolution of valve opening control action to reach the representative operating point ($P_{ref} = 2$ bar, $Q_{r_ref} = 54$ L/h) using inverse local models (blue), and expert control based on fuzzy logic (red).

3.4. Discussion of the Results

The three chosen approaches (ANNs, expert control, and fuzzy-integrated local inverse models) were able to adequately control the MF system, as shown in the previous results subsections. However, the three controllers showed differences in the performance of the dynamic specifications: the speed at which the system reaches the operating point (settling time), and presence of oscillations (overshoot). Some differences were also found in terms of their robustness, and the data required for the development of the controllers (Table 3).

Table 3. Comparison of the control techniques studied.

Controller	Modelling	Control	Robustness
Local models	Few data required	Slow, precise	High. Some problems in different functioning points
Expert control	Only models look-up-table	Sharp, fast, precise	Pondering problems in different working areas
Artificial neural networks	Many data required	Slow, precision achieved by PI controller	Limited. The models do not cover all areas

The ANN-based control had some problems at different operating points showing oscillations that can be attributed to incorrect identification of the dynamics when the network is trained to meet the full range of operating conditions. However, in this case much more data is needed, or a more complex network structure may be required. This implies a higher training effort which may make it difficult to use an adaptive approach.

The control based on fuzzy rules was able to work quickly from the fuzzy rules deduced from the plant operating experience. However, it has the problem that in case of major changes in the system, the expert will be needed again to define the new rules and the whole identification process will have to be repeated.

Local models have the great advantage of requiring less data and expert effort than the other methods for their identification. The settling time is somewhat slower than that achieved by the expert model but sufficient for the studied process. Moreover, compared to the expert models, they allow an easy adaptive implementation of the control, being then the best simplicity-performance trade-off of the AI approaches shown.

4. Conclusions

All three types of regulators implemented were functional and capable of accurately achieving the static specification reference over a wide range of flow and pressure operating conditions. The controllers were also able to function properly during the period when the

system was subjected to a high degree of fouling whenever the membrane of the system was cleaned after each operation. The controllers performed well during experiments in which the cleaning operations were able to avoid high irreversible fouling. Therefore, it can be said that the AI control approaches studied in this work showed very good performance in the control of a MF process.

The proposed control techniques can be applied to different fields: separation in the food industry, membrane bioreactors, membrane medical applications, and laboratory-scale experimentation. The technique to be used in each specific case depends mainly on the information available: ANNs require a lot of experimental data, expert systems require a human expert to be available, and local models require a combination of some expert information and a few data. Dynamic process control requirements may also decide the most appropriate approach, as some techniques are faster than others, in this case expert control being the fastest technique. The same is true for robustness with expert systems providing the best results in this case as well.

Although the proposed control strategies worked well under the conditions of the in the experiments, adaptive versions of the three approaches are desirable and will be developed in the future. Adaptive strategies will allow on-line calibration of the model and controller during operation in the event of irreversible fouling or other changes in the system, such as changes in temperature, pressure, or feed composition. In most situations, the effects on process performance of operating pressure, crossflow velocity, temperature, and pH are complex, highly feed composition dependent, and sometimes weakly explained by physical models. A desirable adaptive control would be able to adjust in minimum time the operating variables seeking to optimize process performance. For example, such controllers can be used in a batch process to adjust pressure and crossflow velocity to minimize the energy required for the concentration stage. Alternatively, they can also be used in continuous processes to jointly optimize the operation phase and the cleaning phase to improve process economics.

Author Contributions: Conceptualization, J.-L.D. and J.M.G.-Z.; methodology, J.-L.D. and J.M.G.-Z.; software, J.-L.D., V.M.-M.; validation, J.-L.D., V.M.-M. and J.M.G.-Z.; formal analysis, J.-L.D., V.M.-M. and J.M.G.-Z.; investigation, J.-L.D. and V.M.-M.; resources, J.-L.D., J.M.G.-Z. and A.S.-M.; data curation, V.M.-M., J.-L.D., J.M.G.-Z. and A.S.-M.; writing—original draft preparation, V.M.-M.; writing—review and editing, J.M.G.-Z. and J.-L.D.; visualization, V.M.-M., J.M.G.-Z. and A.S.-M.; supervision, J.-L.D., J.M.G.-Z. and A.S.-M.; project administration, J.-L.D. and J.M.G.-Z.; All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: To the students Victor Claver, Carlos Blasco, and Sergio Romero, who participated in the set-up and previous developments with the pilot plant used in this work.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Ozgun, H.; Tao, Y.; Ersahin, M.E.; Zhou, Z.; Gimenez, J.B.; Spanjers, H.; van Lier, J.B. Impact of Temperature on Feed-Flow Characteristics and Filtration Performance of an Upflow Anaerobic Sludge Blanket Coupled Ultrafiltration Membrane Treating Municipal Wastewater. *Water Res.* **2015**, *83*, 71–83. [CrossRef] [PubMed]
2. Muñoz Sierra, J.D.; Oosterkamp, M.J.; Wang, W.; Spanjers, H.; van Lier, J.B. Comparative Performance of Upflow Anaerobic Sludge Blanket Reactor and Anaerobic Membrane Bioreactor Treating Phenolic Wastewater: Overcoming High Salinity. *Chem. Eng. J.* **2019**, *366*, 480–490. [CrossRef]
3. Düppenbecker, B.; Engelhart, M.; Cornel, P. Fouling Mitigation in Anaerobic Membrane Bioreactor Using Fluidized Glass Beads: Evaluation Fitness for Purpose of Ceramic Membranes. *J. Memb. Sci.* **2017**, *537*, 69–82. [CrossRef]
4. Armignacco, P.; Garzotto, F.; Bellini, C.; Neri, M.; Lorenzin, A.; Sartori, M.; Ronco, C. Pumps in Wearable Ultrafiltration Devices: Pumps in Wuf Devices. *Blood Purif.* **2015**, *39*, 115–124. [CrossRef]

5. Liu, Y.; Faria, M.; Leonard, E. Spallation of Small Particles from Peristaltic Pump Tube Segments. *Artif. Organs.* **2017**, *41*, 672–677. [CrossRef] [PubMed]
6. Deiringer, N.; Friess, W. Proteins on the Rack: Mechanistic Studies on Protein Particle Formation During Peristaltic Pumping. *J. Pharm. Sci.* **2022**, *111*, 1370–1378. [CrossRef]
7. Kazemi, A.S.; Patterson, B.; LaRue, R.J.; Papangelakis, P.; Yoo, S.M.; Ghosh, R.; Latulippe, D.R. Microscale Parallel-Structured, Cross-Flow Filtration System for Evaluation and Optimization of the Filtration Performance of Hollow-Fiber Membranes. *Sep. Purif. Technol.* **2019**, *215*, 299–307. [CrossRef]
8. Yuan, P.; Le, Z.; Zhong, L.; Huang, C. Dynamic Dialysis: An Efficient Technique for Large-Volume Sample Desalting. *Prep. Biochem. Biotechnol.* **2015**, *45*, 588–595. [CrossRef]
9. McIntyre, M.P.; van Schoor, G.; Uren, K.R.; Kloppers, C.P. Modelling the Pulsatile Flow Rate and Pressure Response of a Roller-Type Peristaltic Pump. *Sens. Actuators A Phys.* **2021**, *325*, 112708. [CrossRef]
10. Gendy, M.E.L.; Anwar Bég, O.; Kadir, A.; Islam, M.N.; Tripathi, D. CFD Simulation and Visualization of Netonian and Non-Newtonian Transport in a Peristaltic Micro-Pump. *J. Mech. Med. Biol.* **2021**, *21*, 2150058. [CrossRef]
11. Medvedev, A.; Hillerström, G. External Model Control of a Peristaltic Pump. *IFAC Proc. Vol.* **1994**, *27*, 517–522. [CrossRef]
12. van der Bruggen, B. Microfiltration, Ultrafiltration, Nanofiltration, Reverse Osmosis, and Forward Osmosis. *Fundam. Modeling Membr. Syst. Membr. Process Perform.* **2018**, *2016*, 25–70. [CrossRef]
13. Iritani, E.; Katagiri, N. Developments of Blocking Filtration Model in Membrane Filtration. *KONA Powder Part. J.* **2016**, *2016*, 179–202. [CrossRef]
14. Kecili, K.; Habarou, H.; Suty, H.; Croué, J.P.; Pontié, M. Approche Analytique Intégrée Du Colmatage de Membranes MF–UF Par Les Matières Organiques Naturelles (MON). Partie 1: Caractérisations in Situ et Modèles de Colmatage. *Comptes Rendus Chim.* **2006**, *9*, 1178–1191. [CrossRef]
15. Sreedhar, N.; Mavukkandy, M.O.; Aminabhavi, T.M.; Hong, S.; Arafat, H.A. Fouling Mechanisms in Ultrafiltration under Constant Flux: Effect of Feed Spacer Design. *Chem. Eng. J.* **2022**, *446*, 136563. [CrossRef]
16. Winzeler, H.B.; Belfort, G. Enhanced Performance for Pressure-Driven Membrane Processes: The Argument for Fluid Instabilities. *J. Memb. Sci.* **1993**, *80*, 35–47. [CrossRef]
17. Flendrig, J.G.; Carpay, W.M.; Dekkers, W.T. The Accurate Control of Ultrafiltration. *Artif. Organs.* **1978**, *2*, 144–146. [CrossRef]
18. Roberts, M.; Winney, R.J. Errors in Fluid Balance with Pump Control of Continuous Hemodialysis. *Int. J. Artif. Organs.* **1992**, *15*, 99–102. [CrossRef]
19. Morales, E.O.; Polycarpou, M.M.; Member, S.; Hemasilpin, N.; Bissler, J.J. Hierarchical Adaptive and Supervisory Control of Continuous Venovenous Hemofiltration. *IEEE Trans. Control. Syst. Technol.* **2001**, *9*, 445–457. [CrossRef]
20. Niu, C.; Li, X.; Dai, R.; Wang, Z. Artificial Intelligence-Incorporated Membrane Fouling Prediction for Membrane-Based Processes in the Past 20 Years: A Critical Review. *Water Res.* **2022**, *216*, 118299. [CrossRef]
21. Jawad, J.; Hawari, A.H.; Javaid Zaidi, S. Artificial Neural Network Modeling of Wastewater Treatment and Desalination Using Membrane Processes: A Review. *Chem. Eng. J.* **2021**, *419*, 129540. [CrossRef]
22. Zhou, Y.; Khan, B.; Gu, H.; Christofides, P.D.; Cohen, Y. Modeling UF Fouling and Backwash in Seawater RO Feedwater Treatment Using Neural Networks with Evolutionary Algorithm and Bayesian Binary Classification. *Desalination* **2021**, *513*, 115129. [CrossRef]
23. Ibáñez, R.; Almécija, C.; Guadix, A.; Guadix, E.M. Modelling the Ultrafiltration of Protein Solutions by Artificial Neural Networks. In *Artificial Neural Networks (Mathematics Research Developments)*; Nova Science Publishers, Inc.: New York, NY, USA, 2011; pp. 361–384. ISBN 9781617615535.
24. Corbatón-Báguena, M.-J.; Vincent-Vela, M.-C.; Gozálvarez-Zafrilla, J.-M.; Álvarez-Blanco, S.; Lora-García, J.; Catalán-Martínez, D. Comparison between Artificial Neural Networks and Hermia’s Models to Assess Ultrafiltration Performance. *Sep. Purif. Technol.* **2016**, *170*, 434–444. [CrossRef]
25. Yusuf, Z.; Wahab, N.A.; Sudin, S. Soft Computing Techniques in Modelling of Membrane Filtration System: A Review. *Desalination Water Treat* **2019**, *161*, 144–155. [CrossRef]
26. Yuan, W.; Kocic, A.; Zydney, A.L. Analysis of Humic Acid Fouling during Microfiltration Using a Pore Blockage–Cake Filtration Model. *J. Memb. Sci.* **2002**, *198*, 51–62. [CrossRef]
27. Yuan, W.; Zydney, A.L. Effects of Solution Environment on Humic Acid Fouling during Microfiltration. *Desalination* **1999**, *122*, 63–76. [CrossRef]
28. Yuan, W.; Zydney, A.L. Humic Acid Fouling during Microfiltration. *J. Memb. Sci.* **1999**, *157*, 1–12. [CrossRef]
29. Gruskevica, K.; Mezule, L. Cleaning Methods for Ceramic Ultrafiltration Membranes Affected by Organic Fouling. *Membranes* **2021**, *11*, 131. [CrossRef]
30. Alresheedi, M.T.; Barbeau, B.; Basu, O.D. Comparisons of NOM Fouling and Cleaning of Ceramic and Polymeric Membranes during Water Treatment. *Sep. Purif. Technol.* **2019**, *209*, 452–460. [CrossRef]
31. Narendra, K.S.; Parthasarathy, K. Identification and Control of Dynamical Systems Using Neural Networks. *IEEE Trans. Neural Netw.* **1990**, *1*, 4–27. [CrossRef]
32. Zadeh, L.A. Fuzzy Sets. *Inf. Control.* **1965**, *8*, 338–353. [CrossRef]
33. Albertos, P.; Olivares, M.; Sala, A. Fuzzy Logic Based Look-up Table Controller with Generalization. *Proc. Am. Control. Conf.* **2000**, *3*, 1949–1953. [CrossRef]

34. Murray-Smith, R.; Johansen, T.A. *The Operating Regime Approach to Nonlinear Modelling and Control*; Taylor and Francis: London, UK, 2020; pp. 3–72. [CrossRef]
35. Bezdek, J.C. *Pattern Recognition with Fuzzy Objective Function Algorithms*; Springer: New York, NY, USA, 1981.



Article

Analysis of Influencing Factors on the Gas Separation Performance of Carbon Molecular Sieve Membrane Using Machine Learning Technique

Yanqiu Pan ¹, Liu He ^{1,2}, Yisu Ren ³, Wei Wang ^{1,*} and Tonghua Wang ¹

¹ School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China; yqpan@dlut.edu.cn (Y.P.); liuhe1992@hotmail.com (L.H.); wangth@dlut.edu.cn (T.W.)

² Jihua Laboratory, Foshan 528000, China

³ Faculty of Science, The University of Melbourne, Melbourne, VIC 3010, Australia; szrenyisu@hotmail.com

* Correspondence: dwwang@dlut.edu.cn

Abstract: Gas separation performance of the carbon molecular sieve (CMS) membrane is influenced by multiple factors including the microstructural characteristics of carbon and gas properties. In this work, the support vector regression (SVR) method as a machine learning technique was applied to the correlation between the gas separation performance, the multiple membrane structure, and gas characteristic factors of the self-manufactured CMS membrane. A simple quantitative index based on the Robeson's upper bound line, which indicated the gas permeability and selectivity simultaneously, was proposed to measure the gas separation performance of CMS membrane. Based on the calculation results, the inferred key factors affecting the gas permeability of CMS membrane were the fractional free volume (FFV) of the precursor, the average interlayer spacing of graphite-like carbon sheet, and the final carbonization temperature. Moreover, the most influential factors for the gas separation performance were supposed to be the two structural factors of precursor influencing the porosity of CMS membrane, the carbon residue and the FFV, and the ratio of the gas kinetic diameters. The results would be helpful to the structural optimization and the separation performance improvement of CMS membrane.

Keywords: carbon molecular sieve membrane; gas separation; machine learning; support vector regression

1. Introduction

Membrane-based gas separation technology has been widely concerned because of its high separation efficiency, environmental friendship, and easy operation [1,2]. In order to broaden the application of the technology, it is important to develop novel membrane materials with excellent gas separation performance [3]. Carbon molecular sieve (CMS) membrane is a carbon-based membrane fabricated from the pyrolysis of polymeric precursor film [4,5]. As a novel membrane for gas separation with a broad development prospect, CMS membrane has the advantages of excellent gas permeability and selectivity, high thermal and chemical stability, and anti-plasticization. The microstructure of CMS membranes varies largely with the choice of precursors and preparation processes, affecting the separation performance [5–8]. Exploring the influence of factors, such as the microstructural characteristics and gas properties, on the gas separation performance, or the so-called permselectivity, would be helpful to the adjustment of the microstructure and the optimization to the membrane preparation. However, gas permeability of CMS membrane is hard to correlate functionally with the plural factors which are not directly interrelated [9–11]. The machine learning technique, which is the core of artificial intelligence, makes it possible to realize the correlation [12,13].

Machine learning is a computational technology to quantitatively predict the relationship between the multiple conditions and the target based on given samples [13,14]. In the fields of biomedicine, chemistry, materials, and the environment, the machine learning technique has been successfully applied to the analysis of the relationship between the characteristics and the performances of materials [15–19]. Specific to membrane-based gas separation, machine learning has been applied to the performance prediction and structural optimization of polymer membranes, zeolite membranes, metal-organic framework membranes, and composite membranes [20–26]. For CMS membrane, Behnia et al. [27] predicted the gas permeability and selectivity through statistical analysis and modeling based on five influential factors, including the type of precursor, blend composition of precursors, final pyrolysis temperature, vacuum pressure during pyrolysis, and operating pressure. The authors concluded that every factor has a significant impact on the gas permeability, especially the final pyrolysis temperature. Based on the actual measurement data of CMS membrane, the machine learning technique is feasible to discuss the influences of structural characteristics, gas properties, and other factors on the gas permeation and separation of CMS membrane.

Several methods based on machine learning techniques were used to analyze the influence of plural factors on specific performance of material based on the obtained data in recent years, such as multiple linear regression, partial least-square, multiple discrimination vector, decision tree, and support vector regression [28–33]. The support vector regression (SVR) method could seek the best compromise between the complexity of the model and the learning ability to obtain the best promotion ability from the limited sample. The SVR method has the following advantages [13,14,28]: (1) for small samples, it could achieve the optimal solution through the existing information; (2) it could get the global optimal solution in theory; and (3) the complexity of the SVR method is independent of the sample dimension. The SVR method is anticipated to effectively analyze the influence of the factors, including structural characteristics and gas properties on the gas separation performance of the CMS membrane based on limited actual characterization results and experimental data.

In this work, the SVR method was applied to the analysis of the multiple factors influencing the gas separation performance of CMS membranes. The data for analysis were collected from the authors' previous work [34–43]. The monomer structure formulas of the polymeric precursors for preparing CMS membranes are shown in Figure S1. The gas permeability and separation performance of CMS membrane were predicted through the factors, and the key influencing factors were determined. The method and results in this work may provide a new insight into the structure-performance relationship of CMS membrane for gas separation.

2. Computational Methods

2.1. Data Collection

Since the existing characterization and measurement data were limited in the category, some structural factors of CMS membranes were substituted by the related ones of precursors. Most permeation coefficients in the previous works were measured at 30 °C and 100 kPa (375 results selected as the sample in this work), and only a small amount of data (24 results) was obtained under other conditions [34–43]. The influence of structural factors and operating conditions was analyzed in the follow-up work.

Table 1 shows the influencing factors to be discussed as the independent variables based on the structural characterization and gas permeability [34–43], including the precursor characteristic, carbonization condition, carbon microstructure, and molecular property of permeated gases. Among the characteristics of polymeric precursors, the fractional free volume (FFV) and the carbon residue influencing the porosity of CMS membrane were selected as the influential factors [44–46], as well as the fraction of sp² carbon and aromatic carbon affecting the arrangement of carbon molecules [47,48]. The pyrolysis temperature, which is particularly applicable to the structural adjustment of CMS membrane, was chosen as an influencing factor [49]. The carbon microstructural factors contained the average

interlayer spacing, length, and thickness of the carbon microcrystal consisting CMS membrane [6,9]. In addition, the gas molecular kinetic diameter related to the resistance, the gas molecular mass affecting the free diffusion, and the gas–carbon interaction potential influencing the gas sorption in CMS membrane were taken into consideration [50–52]. The calculation methods of some factors are depicted in S.2–S.4 of the Supplementary Materials.

Table 1. The selected factors for analyzing the structural–performance relationship of CMS membrane.

Category	Contents
Precursor structure	Fractional free volume (FFV); carbon residue; fraction of sp ² -hybrid carbon; fraction of carbon in aromatic rings
Carbonation condition	Pyrolysis temperature
Carbon microcrystal structure	Average interlayer spacing; length of carbon microcrystal; thickness of carbon microcrystal
Properties of permeated gas molecules	Mass; kinetic diameter; van der Waals potential between gas and carbon

As the performance indicator (dependent variable) of CMS membranes, besides the permeability of gases (CO₂, CH₄, N₂, O₂, and H₂), a quantitative index, named characteristic distance (d), was proposed in this work. Figure 1 shows the concept of d , which was the vertical distance of a black legend away from the Robeson’s upper bound line of a specific gas pair [53,54]. When the legend was above the upper bound line, the d was a positive value; otherwise, the d was negative. The d , as a quantitative index, could measure the gas separation performance of CMS membranes, including permeability and selectivity simultaneously.

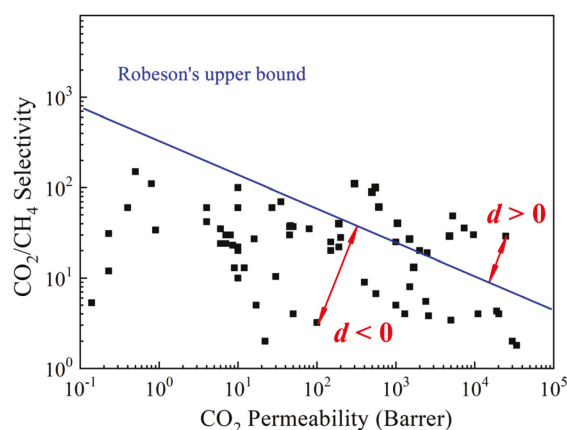


Figure 1. Permselectivity values (characteristic distance d) of the CO₂/CH₄ gas pair based on Robeson’s upper bound [54].

The formula of Robeson upper bound line is [54]:

$$\lg P = \lg k + n \lg \alpha \quad (1)$$

where P (Barrer, 1 Barrer = 10^{-10} cm³(STP)·cm·cm^{−2}·s^{−1}·cmHg^{−1}) is the permeability coefficient of fast gas; α is the selectivity coefficient; and n and $\lg k$ are the slope and intercept of the upper bound line, respectively. In order to make a consistent evaluation standard to different gas pairs, the n and $\lg k$, as shown in Tables S2 and S5 in the Robeson upper bound lines [54], were selected for all gas pairs in the sample.

In order to ensure the comparability between different variables and the reasonability of the regression results, the variable x should be transferred to X with the mean value of 0 and the standard deviation of 1:

$$X = \frac{x - \mu}{\sigma} \quad (2)$$

where μ and σ are the mean value and the standard deviation of the variable x , respectively. The standardized results of the variables are shown in Figure 2, which were used to show the relevance of variables qualitatively and illustrate the independence of them. Obviously, variations of different independent variables with the group number were inconsistent and did not follow a specific variation trend. Thus, it could be considered that the collected data were suitable for calculation.

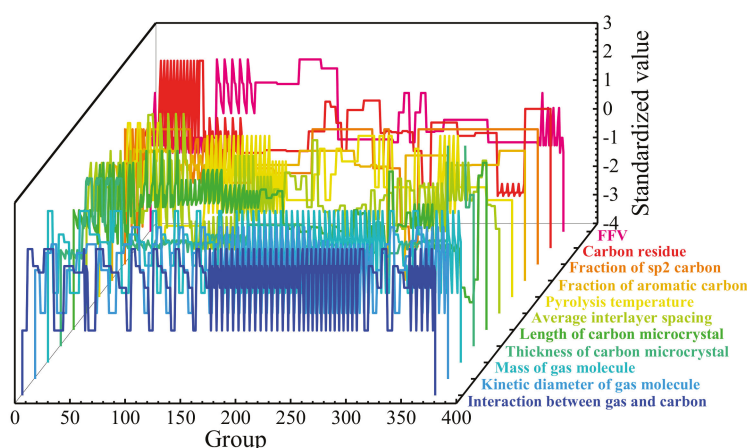


Figure 2. Standardized values of the independent variables.

2.2. SVR Theorem

Figure 3 indicates the basic idea of the SVR method. For independent variables x and dependent variable y , the loss is calculated only if the difference between y and the results predicted from the independent variable $f(x)$ are greater than ε [13]. When $|f(x) - y| < \varepsilon$, the value of $|f(x) - y|$ is treated as zero; otherwise, the value is $|f(x) - y| - \varepsilon$. It is equivalent to building a 2ε wide belt centered on $f(x)$ and the prediction is correct when the sample falls into the belt. The $f(x)$ is called hyperplane, whose geometry is related to the dimension of x . However, the hyperplane may not be constructed in practice due to the characteristics of the sample. Under such circumstances, the samples could be mapped from the original sample space to a higher dimensional feature space in order to realize the linear correlation. The γ is called breadth, which affects the range of action and thereby affects the generalization performance.

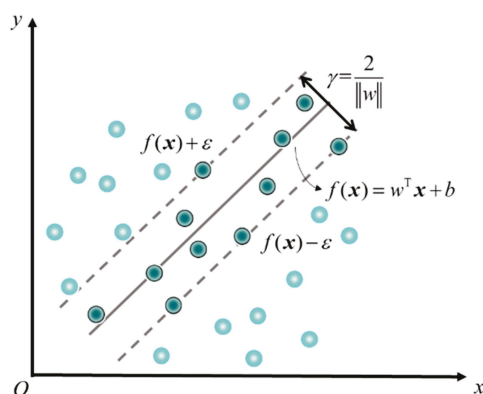


Figure 3. Diagram of SVR theorem.

In the sample space, the hyperplane could be described by:

$$f(x) = w^T x + b \quad (3)$$

where w is the vector of weight (w^T is the transpose of w), and b is the bias term. When the sample needs mapping in order to construct a hyperplane, the original independent x would map into the eigenvector $\Phi(x)$ and the hyperplane function becomes [13,28]:

$$f(x) = w^T \Phi(x) + b \quad (4)$$

The purpose of the SVR is to find the hyperplane with the largest breadth (γ in Figure 3), which is equivalent to find the w satisfying the objective function $\min \|w\|^2/2$ subject to $y_i \cdot (w^T x_i + b) \geq 1$. In practice, however, the hyperplane is difficult to appear in a linear form. There are two ways to make the sample linear regression: adding a penalty coefficient to the objective function and mapping the samples to the higher dimensional space. Then, the objective function of SVR hyperplane becomes:

$$\min_{w, b, \xi_i, \hat{\xi}_i} \left[\frac{\|w\|^2}{2} + C \sum_{i=1}^m (\xi_i + \hat{\xi}_i) \right] \quad (5)$$

$$s.t. \begin{cases} f(x_i) - y_i \leq \varepsilon + \xi_i \\ y_i - f(x_i) \leq \varepsilon + \hat{\xi}_i \\ \xi_i \geq 0, \hat{\xi}_i \geq 0 \end{cases}$$

where C is the penalty coefficient, which is the tolerance for the error. The C should be neither too large nor too small in order to prevent over-fit and under-fit. ξ_i and $\hat{\xi}_i$ are called slack variables, which indicate that the relaxation degree on both sides of the space might be different.

Combined with the rationale of SVR as shown in Figure 3, the solution of the SVR model would be achieved by constructing the Lagrange equation and solving its partial derivative [13]. The Equation (4) could be written in the explicit form:

$$f(x) = \sum_{i=1}^m (\hat{\alpha}_i - \alpha_i) \Phi(x_i)^T \Phi(x) + b \quad (6)$$

where α_i and $\hat{\alpha}_i$ are the Lagrange multipliers. The w would, therefore, be solved and used in the comparison of each influencing factor.

In practice, the kernel function $\kappa(x_i, x_j)$, which is a symmetric and positive definite in the sample space, is constructed to replace the inner product of the mapping eigenvectors:

$$\kappa(x_i, x_j) = \Phi(x_i)^T \Phi(x_j) \quad (7)$$

The kernel function could deal with feature space of arbitrary dimensionality, and the functional form of $\Phi(x_i)$, which is hidden in the kernel function, is unnecessary to calculate explicitly [28,55]. Selecting the kernel function would be helpful to correctly construct the hyperplane in feature space. In this work, the SVR models with linear function, polynomial function, radial basis function (RBF), and Sigmoid function in S.6 (Equations (S13)–(S16)) were built as the kernel functions, and the best model was chosen to analyze the influences of the multiple factors on the gas separation performance of CMS membranes.

3. Analyzing Process of Influencing Factors

Figure 4 depicts the analyzing process of the multiple influencing factors on gas permeation and separation performance of CMS membrane based on the SVR method. First, the obtained data were collected from the references [34–43]. The values of some factors, such as FFV, carbon structural parameters, and gas–carbon interaction, should be calculated through S.2–S.4 of the Supplementary Materials. Next, the data of each factor

were standardized according to Section 2.1, in order to ensure the comparability between any two independent variables. Then, the correlation coefficients were calculated and the independent variables were eliminated with high correlation. After data elimination, the remaining processed data were randomly divided into a training set (the blue dots) and a test set (the red dots) in the proportion of 4:1 [26,29]. During the calculation, the data of the training set were used to train the model, and the test set was calculated by the trained model to test the model's reliability. Finally, the important factors affecting the performance were determined and finally analyzed based on the average weight results of 100 times calculation. The analyzing process on the basis of the SVR method was realized using Python script.

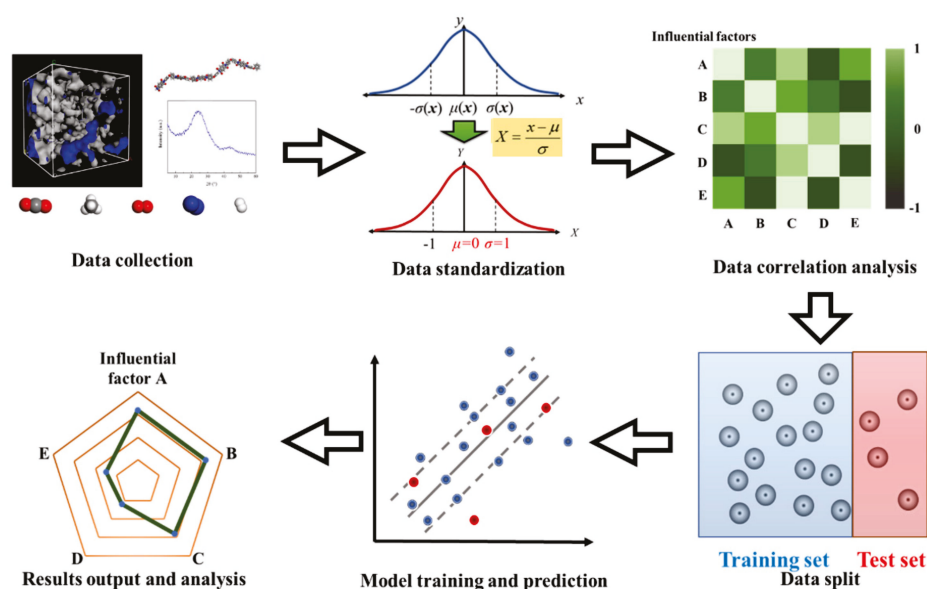


Figure 4. The processing route of influencing factor analysis based on SVR method.

4. Results and Discussion

4.1. Correlation Analysis on the Independent Variables

If the two variables with strong correlation to each other in the sample are simultaneously taken into account in the analysis, the quality of the model may be negatively affected and the regression result would become unreasonable [28]. Before the regression, the correlation coefficient R_s (Equation (8), where the $Cov(x_i, x_j)$ is the covariance of the independent variables x_i and x_j , $\sigma^2(x_i)$ and $\sigma^2(x_j)$ and their variations) were calculated, and one of the variables with large correlation coefficient was removed. The value of the correlation coefficient, which assessed whether to remove the variable, was between 0.8 and 0.9 in the references [28,29,56–58]. In this work, the value was selected as 0.8, which is also the criterion for judging whether two variables are highly correlated [59].

$$R(x_i, x_j) = \frac{Cov(x_i, x_j)}{\sqrt{\sigma^2(x_i)\sigma^2(x_j)}} \quad (8)$$

Figure 5 shows the heatmap depicting the calculation results of the correlation coefficients between every two independent variables in the sample data. All the correlation coefficients were less than 0.8. Therefore, no variable was deleted in the processes of model establishing, training, and predicting.

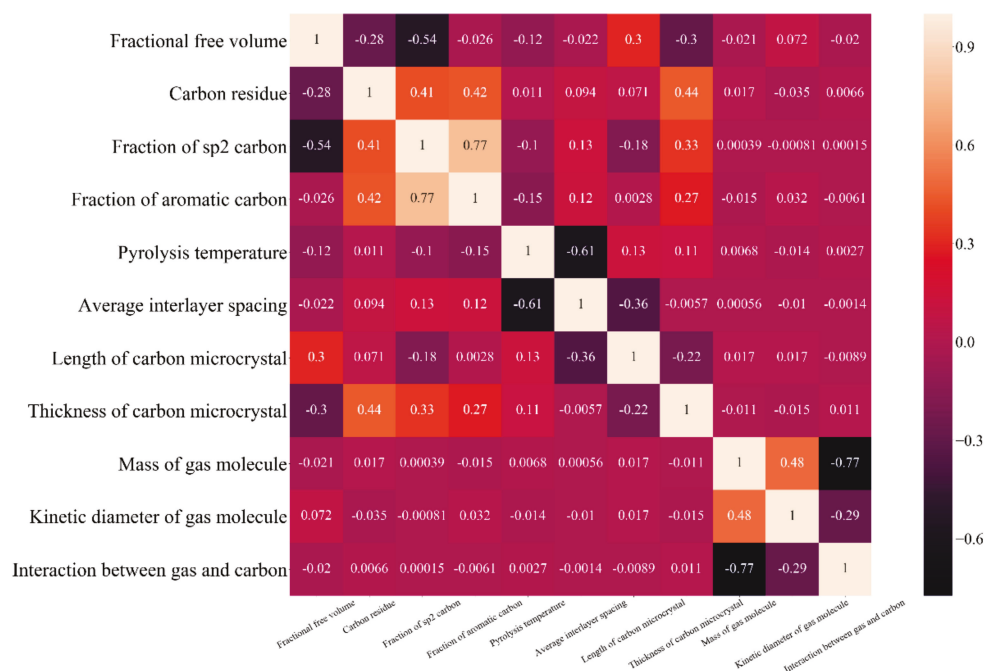


Figure 5. Heatmap of the correlation coefficients between independent variations.

4.2. Model Reliability and Parameter Optimization

In order to validate the reliability of the SVR method in the correlation of the influencing factors and gas permeability of CMS membranes, the SVR method with four kinds of kernel function and three classical multiple linear regression (MLR) methods (simple linear regression, Ridge regression, and Lasso regression) were, respectively, used for the regression between the influential factors and the gas permeability of CMS membranes. Three statistical indicators between the calculation results and the experimental data, including the determination coefficient (R^2 , Equation (9)), root mean square error ($RMSE$, Equation (10)), and mean absolute error (MAE , Equation (11)), were calculated in order to compare the regression effect of each method.

$$R^2 = 1 - \frac{\sum_{i=1}^m [y_i - f(x_i)]^2}{\sum_{i=1}^m (y_i - \bar{y})^2} \quad (9)$$

$$RMSE = \sqrt{\frac{1}{m} \sum_{i=1}^m [y_i - f(x_i)]^2} \quad (10)$$

$$MAE = \frac{1}{m} \sum_{i=1}^m |y_i - f(x_i)| \quad (11)$$

where y_i and $f(x_i)$ are, respectively, the actual dependent variable and the calculated result based on the independent variable of the i th sample; $\bar{y}$ is the mean value of the actual dependent variable; and m is the number of samples. The R^2 , $RMSE$, and MAE of the gas permeabilities between the experimental data and the predicted values by SVR and MLR methods were calculated, and the accuracies of these methods were determined by the calculated results.

Tables 2 and 3 list the statistical indicators calculated by the SVR method and the MLR method, respectively, based on the experimental data from the authors' previous work [34–43]. The calculated indicators of the SVR method, except for the one of the models with the sigmoid kernel, exhibited larger R^2 , smaller $RMSE$, and smaller MAE than the ones of the MLR method. This indicates that the SVR method with global optimality

may correlate the influencing factors and the permeability of the CMS membrane more accurately. In addition, the models with the RBF kernel and the polynomial kernel showed similar regression effects on the influencing factors and the gas permeability of the CMS membrane, but the models with the linear kernel and the sigmoid kernel could not correlate the influencing factors and the performances well. The model with the RBF kernel, which is less complex and could realize non-linear mapping, is slightly better than the one with the polynomial kernel and is more suitable for the regression in this work.

Table 2. Statistical indicators of the results calculated by SVR models.

Kernel Function	R^2	RMSE	MAE
RBF	0.794	0.281	0.139
Polynomial	0.730	0.321	0.181
Linear	0.303	0.516	0.209
Sigmoid	−8.562	1.913	1.375

Table 3. Statistical indicators of the results calculated by MLR models.

Regression Method	R^2	RMSE	MAE
Linear	0.201	0.553	0.387
Ridge	0.204	0.552	0.386
Lasso	−0.060	0.637	0.409

In order to improve the regression performance of the SVR models with the RBF kernel and the polynomial kernel, the parameters of the models needed to be modified. As for the model with the RBF kernel, the penalty coefficient (C) in Equation (5) and the breadth (γ) in Figure 3 were optimized. The polynomial degree of the polynomial kernel function also needed to be adjusted. The variations of statistical indicators with the model parameters are shown in Figure S3 and Figure S7. Aiming at larger R^2 while avoiding both over-fit and under-fit, $C = 5$ and $\gamma = 0.3$ were finally selected as the parameters of the SVR model with the RBF kernel and the quadric polynomial kernel, respectively.

4.3. Analysis of the Influencing Factors

4.3.1. Factors Influencing Gas Permeability

The SVR models after parameter modification were used as the analytical models to regress the sample data and predict the gas permeability of the CMS membrane.

1. Regression results

Figure 6 shows the comparison between the predicted results regressed by the SVR analytical models with two kernel functions and the experimental data of the gas permeability from all the precursors presented in Figure S1 [34–43]. The scatter points were evenly distributed on both sides of the diagonal, which indicated that the experimental data and the corresponding predicted values were close to each other.

Table 4 depicts the statistical indicators based on the regression results in Figure 6. Compared with the results in Table 2, the larger R^2 and smaller MAE in Table 4 indicated that selecting the appropriate kernel function and optimizing the suitable parameters was important to improve the regression effect. The larger RMSEs in Table 4 was probably because a small number of data points were not predicted accurately in order to ensure the overall regression effect. The R^2 of both models with optimized parameters were larger than 0.8, which revealed the high correlation between the results calculated by the SVR models after parameter adjustment and the experimental data. In addition, the regression effect of the SVR model with RBF kernel was better for the regression, due to the larger R^2 and smaller RMSE and MAE.

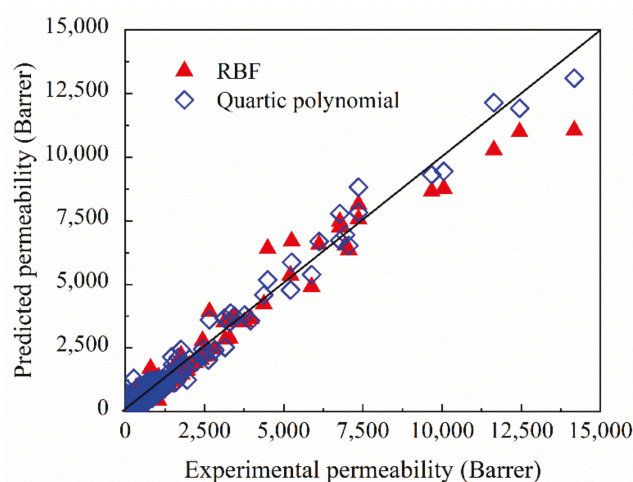


Figure 6. Comparison between predicted results and experimental data of the gas permeability by SVR method.

Table 4. Statistical indicators of the results calculated by SVR analytical models.

Kernel Function	R^2	RMSE	MAE
RBF	0.841	0.413	0.129
Quartic polynomial	0.809	0.419	0.156

2. Influencing factors analysis

The radar map (Figure 7) was applied to represent the absolute values of the normalized weights for each influencing factor (calculated by $|w_i| / \sum |w_i|$, where w_i is the original weight of the independent variable i). The factors with underline, which had a negative weight value, were negatively related to the permeability according to Equations (3) and (4), and were shown in absolute value in the radar map in order to realize an intuitive comparison among the weight of each independent variable. Moreover, the weights of the independent variables corresponding to the SVR models with the RBF kernel and the quartic polynomial kernel were different.

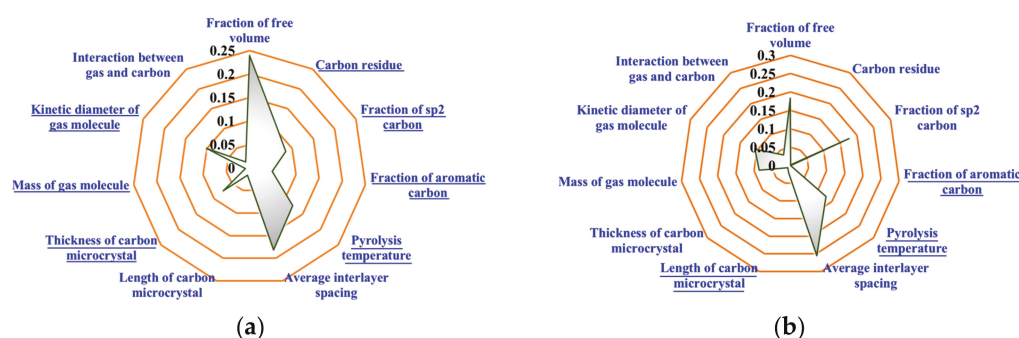


Figure 7. The normalized weights of the influencing factors on gas permeability regressed by SVR model with (a) RBF kernel; (b) quartic polynomial kernel (factors with underline are negative).

Figure 7a shows the regression result of the SVR model with the RBF kernel, which indicates that the main factors affecting the gas permeability of CMS membrane are the FFV of precursor, the average interlayer spacing, and the pyrolysis temperature. The precursor with the higher FFV would convert into the CMS membrane with a more developed microporous structure for gas transport and, therefore, the CMS membrane has higher gas permeability [44]. This is consistent with the experimental results in the previous work on the CMS membrane preparations from different precursors [36]. The average interlayer

spacing could reflect the pore size of the CMS membrane to a certain extent. Wider interlayer spacing in the carbon matrix corresponded to a larger-sized micropore [36–38,42], which caused less hindrance to the gas molecules [50]. Higher final pyrolysis temperature would lead to a more thorough thermal condensation and a greater degree of shrinkage for the CMS membrane [9]. The SVR model with the RBF kernel could more reasonably determine the influences of each independent variable on gas permeability.

Figure 7b shows the regression by the model with the quartic polynomial kernel. The calculated results may be unreasonable because the weight of the factor “mass of gas molecule” was positive to the gas permeability. The gas permeability equals the product of gas adsorbability and gas diffusivity. The adsorbability has little relation to the molecule mass [5,8], while the diffusivity of gas molecule is inversely proportional to the square root of its molar mass in general [51], which indicates that the molar mass of gas should negatively relate to the gas permeability. Therefore, the SVR model with the quartic polynomial kernel may not be suitable for the analysis of influencing factors on the gas separation performance of CMS membrane.

According to Figure 7a, showing the regression results by the SVR model with the RBF kernel, it could also be found that the weights of the gas properties were smaller than those of structural factors. Although the permeability of different gases in one CMS membrane varies greatly, the influences of membrane structure on the performance are stronger than those of gas properties regarding gas permeation. That is to say, the permeability of slow gas in the CMS membrane with a suitable structure would be higher than the one of fast gas in the membrane with a poor structure.

4.3.2. Factors Influencing Gas Separation Performance

The SVR model with the RBF kernel, whose regression result of the gas permeability was more reasonable in Section 4.3.1, was selected to regress multiple factors to the characteristic distance (d) and resolve the weights in order to determine and analyze the key influential factors.

1. Regression results

Figure 8 shows the comparison of the characteristic distance between the predicted results and the experimental data from all the precursors in Figure S1 [34–43]. The data points in Figure 8 were evenly distributed on the value domain and exhibited good representativeness, while the data points in Figure 6 were mostly concentrated on one side. The R^2 , $RMSE$, and MAE calculated from the predicted results and the experimental data were 0.932, 0.260, and 0.165, respectively, which indicated the reliability of the model.

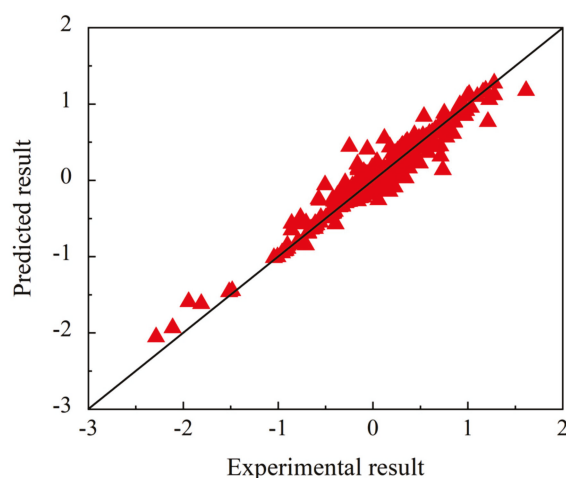


Figure 8. Comparison between predicted and experimental results of characteristic distance.

2. Influencing factors analysis

Figure 9 shows the absolute values of the normalized weights. The most important factor influencing the synthetic gas permeation and separation performance is the porosity of the CMS membrane. The porosity is controlled by the carbon residue and the FFV of precursor, as well as the ratio between the kinetic diameters of the fast component and the slow component in the gas pair for separation. The smaller carbon residue of CMS membrane indicates that more small molecular groups would escape from the solid matrix during the thermal decomposition and more micropores would be created [42]. Such a structure is conducive to the transport of gas molecules in the CMS membrane, especially the fast gas [45,46]. Higher porosity corresponds to the larger FFV of the precursor, which is helpful to the gas permeation and separation of the CMS membrane [8,36]. The ratio of kinetic diameter, compared with other properties of gas molecules, is more influential, which manifests that the gap of effective diffusion between different gas molecules in the nanoscale micropores is the main reason for the selectivity of the CMS membrane. The analysis results according to Figure 9 could be helpful to the structural optimization and the separation performance improvement in the CMS membrane.

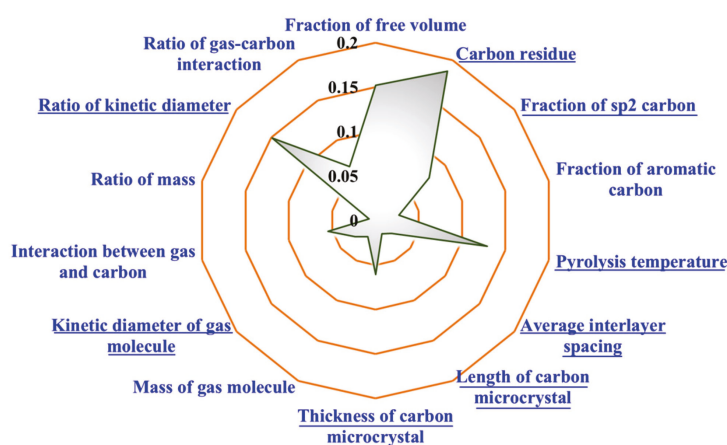


Figure 9. The normalized weight of the influencing factors on characteristic distance (factors with underline are negative).

In addition, the weight of the average interlayer distance is relatively smaller than the one in Figure 7a. Increasing the interlayer distance, which would simultaneously increase the gas permeability of both fast gas and slow gas, may decline the selectivity of the gas pair which, thereby, has no significant effect on the gas separation performance of CMS membrane. The key influencing factors, i.e., the carbon residue and the FFV, are both related to the porosity of CMS membrane, as discussed above [44–46]. In order to improve the performance of gas permeation and selection comprehensively, priority should be given to increasing the porosity of materials of the CMS membrane if the structural parameters that need to be adjusted cannot reach the optimal level together. For the gas pairs with specific components, the interlayer spacing could be adjusted appropriately according to the kinetic diameter of gas molecules in order to improve the permeability.

5. Conclusions

The SVR method based on the machine learning technique was used to evaluate the relationship between the influencing factors and gas separation performance of self-manufactured CMS membrane. A simple index (d) based on the Robeson's upper-bound line was put forward to quantitatively evaluate the gas separation performance of the CMS membrane, including both permeability and selectivity. Compared with the classical MLR method, the SVR method with the RBF kernel could acquire more accurate results. The main factors affecting the gas permeability of the CMS membrane are the FFV of the precursor, the average interlayer spacing of graphite-like carbon sheets, and the final

carbonization temperature. The performance of gas permeability depends more on the structural characteristics than the properties of gas molecules. A reasonable structure design is the key to improve the gas permeability of the CMS membrane. The main factors affecting the gas separation performance of the CMS membrane are the carbon residue, the FFV of the precursor, and the ratio of gas kinetic diameters. If adjusting the structural parameters cannot reach the optimal performance, increasing the porosity of the CMS membrane could be preferentially considered by increasing the space for the transport of gas molecules.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/membranes12010100/s1>, Figure S1: Chemical structures of precursors, Figure S2: Calculation of fractional free volume (FFV), Figure S3: Calculation of carbon structural parameters, Figure S4: Calculation of gas-carbon interaction, Tables S2 and S5: Parameters of gas pairs in the Robeson upper bound, Figure S6: The kernel functions used in the support vector regression, Figures S3 and S7: Variation of the statistical coefficients with the parameters of the kernel function.

Author Contributions: Conceptualization, Y.P. and L.H.; Formal analysis, L.H., Y.P. and W.W.; Funding acquisition, Y.P.; Investigation, L.H. and Y.P.; Methodology, W.W.; Resources, Y.P. and T.W.; Software, L.H.; Supervision, Y.P. and W.W.; Validation, Y.P. and Y.R.; Visualization, L.H. and Y.R.; Writing—original draft preparation, L.H.; Writing—review and editing, W.W. All authors have read and agreed to the published version of the manuscript.

Funding: This work was funded by the Fundamental Research Funds for the Central Universities, grant number DUT17JC07.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Miricioiu, M.G.; Niculescu, V.-C.; Filote, C.; Raboaca, M.S.; Nechifor, G. Coal Fly Ash Derived Silica Nanomaterial for MMMs-Application in CO₂/CH₄ Separation. *Membranes* **2021**, *11*, 78. [CrossRef] [PubMed]
2. Nemestothy, N.; Bakonyi, P.; Lajtai-Szabo, P.; Belafi-Bako, K. The Impact of Various Natural Gas Contaminant Exposures on CO₂/CH₄ Separation by a Polyimide Membrane. *Membranes* **2020**, *10*, 324. [CrossRef] [PubMed]
3. Li, L.; Xu, R.; Song, C.; Zhang, B.; Liu, Q.; Wang, T. A Review on the Progress in Nanoparticle/C Hybrid CMS Membranes for Gas Separation. *Membranes* **2018**, *8*, 134. [CrossRef] [PubMed]
4. Kim, S.-J.; Kwon, Y.; Kim, D.; Park, H.; Cho, Y.H.; Nam, S.-E.; Park, Y.-I. A Review on Polymer Precursors of Carbon Molecular Sieve Membranes for Olefin/Paraffin Separation. *Membranes* **2021**, *11*, 482. [CrossRef]
5. Adams, J.S.; Itta, A.K.; Zhang, C.; Wenz, G.B.; Sanyal, O.; Koros, W.J. New Insights into Structural Evolution in Carbon Molecular Sieve Membranes during Pyrolysis. *Carbon* **2019**, *141*, 238–246. [CrossRef]
6. Hazazi, K.; Ma, X.; Wang, Y.; Ogieglo, W.; Alhazmi, A.; Han, Y.; Pinnau, I. Ultra-Selective Carbon Molecular Sieve Membranes for Natural Gas Separations Based on a Carbon-Rich Intrinsically Microporous Polyimide Precursor. *J. Membr. Sci.* **2019**, *585*, 1–9. [CrossRef]
7. Chuah, C.Y.; Lee, J.; Song, J.; Bae, T.-H. Carbon Molecular Sieve Membranes Comprising Graphene Oxides and Porous Carbon for CO₂/N₂ Separation. *Membranes* **2021**, *11*, 284. [CrossRef]
8. Xu, R.S.; He, L.; Li, L.; Hou, M.; Wang, Y.; Zhang, B.; Liang, C.; Wang, T. Ultrasensitive Carbon Molecular Sieve Membrane for Hydrogen Purification. *J. Energy Chem.* **2020**, *50*, 16–24. [CrossRef]
9. Wang, T.H.; Zhang, B.; Qiu, J.S.; Wu, Y.H.; Zhang, S.H.; Cao, Y.M. Effects of Sulfone/Ketone in Poly (Phthalazinone Ether Sulfone Ketone) on the Gas Permeation of Their Derived Carbon Membranes. *J. Membr. Sci.* **2009**, *330*, 319–325. [CrossRef]
10. Pan, Y.; He, L.; Wang, W.; Wang, T.; Yu, L. Zigzag Pore Based Molecular Simulation on the Separation of CO₂/CH₄ Mixture by Carbon Membrane. *Can. J. Chem. Eng.* **2019**, *97*, 727–733. [CrossRef]
11. He, L.; Pan, Y.; Wang, T.; Yu, L. Molecular Simulation and Optimization on the Microporous Structure in Carbon Molecular Sieve Membrane for CO₂/CH₄ Separation. *Chem. Phys. Lett.* **2020**, *738*, 136910. [CrossRef]
12. Vapnik, V.N. *Estimation of Dependencies Based on Empirical Data*; Springer-Verlag: Berlin/Heidelberg, Germany, 1982.
13. Vapnik, V.N. *Statistical Learning Theory*; Wiley: New York, NY, USA, 1998.

14. Cherkassky, V.S.; Mulier, F.M. *Learning From Data: Concepts, Theory, and Methods*, 2nd ed.; John Wiley & Sons: Hoboken, NJ, USA, 2007.
15. Ojha, P.K.; Roy, K. Development of a Robust and Validated 2D-QSPR Model for Sweetness Potency of Diverse Functional Organic Molecules. *Food Chem. Toxicol.* **2018**, *112*, 551–562. [CrossRef]
16. Won, S.H.; Haas, F.M.; Dooley, S.; Edwards, T.; Dryer, F. Reconstruction of Chemical Structure of Real Fuel by Surrogate Formulation Based upon Combustion Property Targets. *Combust. Flame* **2017**, *183*, 39–49. [CrossRef]
17. Yan, F.; He, W.; Jia, Q.; Wang, Q.; Xia, S.; Ma, P. Prediction of Ionic Liquids Viscosity at Variable Temperatures and Pressures. *Chem. Eng. Sci.* **2018**, *184*, 134–140. [CrossRef]
18. Xu, X.Y.; Li, L.; Yan, F.Y.; Jia, Q.; Wang, Q.; Ma, P. Predicting Solubility of Fullerene C-60 in Diverse Organic Solvents using Norm Indexes. *J. Mol. Liq.* **2016**, *223*, 603–610. [CrossRef]
19. Mansouri, K.; Grulke, C.M.; Judson, R.S.; Williams, A.J. OPERA Models for Predicting Physicochemical Properties and Environmental Fate Endpoints. *J. Cheminform.* **2018**, *10*, 10. [CrossRef]
20. Ahmad, A.L.; Adewole, J.K.; Leo, C.P.; Ismail, S.; Sultan, A.S.; Olatunji, S.O. Prediction of Plasticization Pressure of Polymeric Membranes for CO₂ Removal from Natural Gas. *J. Membr. Sci.* **2015**, *480*, 39–46. [CrossRef]
21. Dehkordi, J.A.; Hosseini, S.S.; Kundu, P.K.; Tan, N.R. Mathematical Modeling of Natural Gas Separation Using Hollow Fiber Membrane Modules by Application of Finite Element Method through Statistical Analysis. *Chem. Prod. Process Model.* **2016**, *11*, 11–15. [CrossRef]
22. Ng, L.Y.; Leo, C.P.; Mohammad, A.W. Optimizing the Incorporation of Silica Nanoparticles in Polysulfone/Poly(vinyl alcohol) Membranes with Response Surface Methodology. *J. Appl. Polym. Sci.* **2011**, *121*, 1804–1814. [CrossRef]
23. Mubashir, M.; Yeong, Y.F.; Lau, K.K. Ultrasonic-Assisted Secondary Growth of Deca-Dodecyl 3 Rhombohedral (DD3R) Membrane and Its Process Optimization Studies in CO₂/CH₄ Separation using Response Surface Methodology. *J. Nat. Gas Sci. Eng.* **2016**, *30*, 50–63. [CrossRef]
24. Chew, T.L.; Ahmad, A.L.; Bhatia, S. Microwave Heating-Synthesized Zeolite Membrane for CO₂/CH₄ Separation. *Desalin. Water Treat.* **2012**, *47*, 139–149. [CrossRef]
25. Rezakazemi, M.; Azarafa, A.; Dashti, A.; Shirazian, S. Development of Hybrid Models for Prediction of Gas Permeation through FS/POSS/PDMS Nanocomposite Membranes. *Int. J. Hydrog. Energy* **2018**, *43*, 17283–17294. [CrossRef]
26. Yang, W.; Liang, H.; Peng, F.; Liu, Z.; Liu, J.; Qiao, Z. Computational Screening of Metal-Organic Framework Membranes for the Separation of 15 Gas Mixtures. *Nanomaterials* **2019**, *9*, 467. [CrossRef] [PubMed]
27. Behnia, N.; Pirouzfar, V. Effect of Operating Pressure and Pyrolysis Conditions on the Performance of Carbon Membranes for CO₂/CH₄ and O₂/N₂ Separation Derived from Polybenzimidazole/Matrimid and UIP-S Precursor Blends. *Polym. Bull.* **2018**, *75*, 4341–4358. [CrossRef]
28. Yang, S.S.; Lu, W.C.; Chen, N.Y.; Hu, Q.N. Support Vector Regression Based QSPR for the Prediction of Some Physicochemical Properties of Alkyl Benzenes. *J. Mol. Struct. THEOCHEM* **2005**, *719*, 119–127. [CrossRef]
29. Qin, Z.J.; Xi, Y.; Zhang, S.D.; Tu, G.P.; Yan, A.X. Classification of Cyclooxygenase-2 Inhibitors Using Support Vector Machine and Random Forest Methods. *J. Chem Inf. Model.* **2019**, *59*, 1988–2008. [CrossRef]
30. Chau, Y.T.; Yap, C.W. Quantitative Nanostructure-Activity Relationship modelling of nanoparticles. *RSC Adv.* **2012**, *2*, 8489–8496. [CrossRef]
31. Li, H.; Cui, Y.; Liu, Y.; Li, W.; Shi, Y.; Fang, C.; Li, H.; Gao, T.; Hu, L.; Lu, Y. Ensemble Learning for Overall Power Conversion Efficiency of the All-Organic Dye-Sensitized Solar Cells. *IEEE Access* **2018**, *6*, 34118–34126. [CrossRef]
32. Shi, Z.; Liang, H.; Yang, W.; Liu, J.; Liu, Z.; Qiao, Z. Machine learning and In Silico Discovery of Metal-Organic Frameworks: Methanol as a Working Fluid in Adsorption-Driven Heat Pumps and Chillers. *Chem. Eng. Sci.* **2020**, *214*, 115430. [CrossRef]
33. Yu, X.; Yu, R. Prediction of the Q-E Parameters from Transition State Structures. *Polym. Eng. Sci.* **2013**, *53*, 2151–2158. [CrossRef]
34. Chen, A. The CO₂ Adsorption and Diffusion Performances in Carbon Membrane. Master's Thesis, Dalian University of Technology, Dalian, China, 2012.
35. Qi, W. Effects of Precursor Chemical Structure on the Microstructure and Gas Permeability of Carbon Membrane. Master's Thesis, Dalian University of Technology, Dalian, China, 2011.
36. Song, J. Carbon Molecular Sieve Membranes Derived from Polyimides for Gas Separation. Master's Thesis, Dalian University of Technology, Dalian, China, 2017.
37. Xu, J. Effects of the Precursor Molecular Weight and ZSM-5 Addition on the Microstructure and Gas Permeability of Carbon Membrane. Master's Thesis, Dalian University of Technology, Dalian, China, 2013.
38. Li, L. Preparation, Pyrolysis Mechanism and Structure Modification of Polyimide Based Carbon Membrane. Ph.D. Thesis, Dalian University of Technology, Dalian, China, 2013.
39. Hu, L. The Studies of Polyetherimide-based Pyrolytic Membrane by Low-Temperature and Carbon Membrane. Master's Thesis, Dalian University of Technology, Dalian, China, 2007.
40. Liu, S. Preoxidation Mechanism of Poly(Phthalazone Ether Sulfone Ketone)s and Preparation Technology Optimization of Their Carbon Membranes. Ph.D. Thesis, Dalian University of Technology, Dalian, China, 2008.
41. Pang, J. Effect of Different Solvents and Drying Methods on Structure and Gas Properties of Carbon Membranes. Master's Thesis, Dalian University of Technology, Dalian, China, 2010.

42. Zhang, B. Preparation, Microstructure and Gas Separation Performance of Molecular Sieving Carbon Membranes. Ph.D. Thesis, Dalian University of Technology, Dalian, China, 2007.
43. Wang, X. The Preparation and Structure Properties of Carbon Membranes derived from Poly (Furfuryl Alcohol) for Gas Separation. Master's Thesis, Dalian University of Technology, Dalian, China, 2007.
44. Singh-Ghosal, A.; Koros, W.J. Air Separation Properties of Flat Sheet Homogeneous Pyrolytic Carbon Membranes. *J. Membr. Sci.* **2000**, *174*, 177–188. [CrossRef]
45. Fu, S.; Sanders, E.S.; Kulkarni, S.S.; Koros, W.J. Carbon Molecular Sieve Membrane Structure-Property Relationships for Four Novel 6FDA Based Polyimide Precursors. *J. Membr. Sci.* **2015**, *487*, 60–73. [CrossRef]
46. Rungta, M.; Xu, L.; Koros, W.J. Structure-Performance Characterization for Carbon Molecular Sieve Membranes using Molecular Scale Gas Probes. *Carbon* **2015**, *85*, 429–442. [CrossRef]
47. Sazali, N.; Salleh, W.N.W.; Nordin, N.A.H.M.; Harun, Z.; Ismail, A.F. Matrimid-Based Carbon Tubular Membranes: The Effect of the Polymer Composition. *J. Appl. Polym. Sci.* **2015**, *132*, 132. [CrossRef]
48. Hu, C.-P.; Polintan, C.K.; Tayo, L.L.; Chou, S.-C.; Tsai, H.-A.; Hung, W.-S.; Hu, C.-C.; Lee, K.-R.; Lai, J.-Y. The Gas Separation Performance Adjustment of Carbon Molecular Sieve Membrane Depending on the Chain Rigidity and Free Volume Characteristic of the Polymeric Precursor. *Carbon* **2019**, *143*, 343–351. [CrossRef]
49. Fu, S.; Wenz, G.B.; Sanders, E.S.; Kulkarni, S.S.; Qiu, W.; Ma, C.; Koros, W.J. Effects of Pyrolysis Conditions on Gas Separation Properties of 6FDA/DETDA:DABA(3:2) Derived Carbon Molecular Sieve Membranes. *J. Membr. Sci.* **2016**, *520*, 699–711. [CrossRef]
50. Rungta, M.; Wenz, G.B.; Zhang, C.; Xu, L.; Qiu, W.; Adams, J.S.; Koros, W.J. Carbon Molecular Sieve Structure Development and Membrane Performance Relationships. *Carbon* **2017**, *115*, 237–248. [CrossRef]
51. Bird, R.B.; Stewart, W.E.; Lightfoot, E.N. *Transport Phenomena*, 2nd ed.; John Wiley & Sons: New York, NY, USA, 2002.
52. Laurendeau, N.M. *Statistical Thermodynamics: Fundamentals and Applications*; Cambridge University Press: Cambridge, UK, 2005.
53. Robeson, L.M. Correlation of Separation Factor Versus Permeability for Polymeric Membranes. *J. Membr. Sci.* **1991**, *62*, 165–185. [CrossRef]
54. Robeson, L.M. The Upper Bound Revisited. *J. Membr. Sci.* **2008**, *320*, 390–400. [CrossRef]
55. Tang, F.; Chen, M.; Wnag, Z. New Approach to Training Support Vector Machine. *J. Syst. Eng. Electron.* **2006**, *17*, 200–205. [CrossRef]
56. Ambe, K.; Ishihara, K.; Ochibe, T.; Ohya, K.; Tamura, S.; Inoue, K.; Yoshida, M.; Tohkin, M. In Silico Prediction of Chemical-Induced Hepatocellular Hypertrophy Using Molecular Descriptors. *Toxicol. Sci.* **2017**, *162*, 667–675. [CrossRef] [PubMed]
57. Dashtbozorgi, Z.; Golmohammadi, H.; Khooshechin, S. QSPR Models for Prediction of Bovine Serum Albumin-Water Partition Coefficients of Organic Compounds and Drugs Based on Enhanced Replacement Method and Support Vector Machine. *Comput. Toxicol.* **2017**, *4*, 1–10. [CrossRef]
58. Yang, Q.; Sun, D.-W.; Cheng, W. Development of Simplified Models for Nondestructive Hyperspectral Imaging Monitoring of TVB-N Contents in Cured Meat during Drying Process. *J. Food Eng.* **2017**, *192*, 53–60. [CrossRef]
59. Utts, J.M.; Heckard, R.F. *Mind on Statistics*, 5th ed.; Cengage Learning: Stamford, CT, USA, 2013.

Article

Modeling and Optimization of Gas Sparging-Assisted Bacterial Cultivation Broth Microfiltration by Response Surface Methodology and Genetic Algorithm

Aleksandar Jokić, Ivana Pajčin *, Nataša Lukić, Vanja Vlajkov, Arpad Kiralj, Selena Dmitrović and Jovana Grahovac *

Faculty of Technology Novi Sad, University of Novi Sad, Bulevar cara Lazara 1, 21000 Novi Sad, Serbia; jokic@uns.ac.rs (A.J.); nlukic@tf.uns.ac.rs (N.L.); vanja.vlajkov@uns.ac.rs (V.V.); arpadkiralj@uns.ac.rs (A.K.); selena.dmitrovic@uns.ac.rs (S.D.)

* Correspondence: ivana.pajcin@uns.ac.rs (I.P.); johana@uns.ac.rs (J.G.)

Abstract: Production of highly efficient biomass-based microbial biopesticides significantly depends on downstream processing in terms of obtaining as high concentration of viable cells as possible. Microfiltration is one of the recommended operations for microbial biomass separation, but its main limitation is permeate flux decrease due to the membrane fouling. The effect of air sparging as a hydrodynamic technique for improvement of permeate flux during microfiltration of *Bacillus velezensis* cultivation broth was investigated. Modeling of the microfiltration was performed using the response surface methodology, while desirability function approach and genetic algorithm were applied for optimization, i.e., maximization of permeate flux and minimization of specific energy consumption. The results have revealed antagonistic relationship between the investigated dependent variables. The optimized values of superficial feed velocity and transmembrane pressure were close to the mean values of the investigated value ranges (0.68 bar and 0.96 m/s, respectively), while the optimized value of superficial air velocity had a more narrow distribution around 0.25 m/s. The results of this study have revealed a significant improvement of microfiltration performance by applying air sparging, thus this flux improvement method should be further investigated in downstream processing of different bacterial cultivation broths.

Keywords: microfiltration; gas sparging; response surface methodology; desirability function; genetic algorithm; permeate flux; specific energy consumption; microbial biopesticide; *Bacillus velezensis*

1. Introduction

Nowadays, conventional agriculture often depends on chemical pesticides and inorganic fertilizers in order to achieve stable and great quantity agricultural output. An environmental concern as a result of the extensive use of agrochemicals has led to development of sustainable agriculture approach [1]. Microbial biopesticides offer an environment-friendly biotechnological alternative to chemical control of plant diseases and pests [2,3]. Utilization of microorganisms or their metabolites in biological control of various plant pathogens represents a fast-growing sector, with expected continued growth in the following years, mostly due to inevitable and necessary development of organic and regenerative agriculture [4,5]. Bacteria of the genus *Bacillus* could be found in the majority of commercially available products for plant protection due to their favorable characteristics for active component of microbial biopesticide [6–8]. *Bacillus velezensis* has been investigated in biological control of different plant diseases considering the ability of *Bacillus velezensis* strains to produce antimicrobial compounds and express mechanisms related to plant growth promotion [9,10]. *Bacillus velezensis* IP22 is a novel biocontrol agent, which expresses several mechanisms of antimicrobial action against

plant pathogens, including competition for growth space and nutrients, as well as production of lipopeptides [11,12]. Sustainable, environment-friendly, and cost-effective production of biopesticides significantly depends on the method of cultivation broth downstream processing [13]. Cell harvesting, i.e., cultivation broth clarification, is the step in downstream processing with an aim of a solid/liquid separation to recover the microbial cells from their suspending medium in order to increase concentration of the active component in the final biopesticide product. In biotechnological production of biopesticides, it is usually done by centrifugation or microfiltration [14]. The effective recovery of the cultivation broth components, especially microbial biomass considering necessity to maintain cell viability, is the penultimate step in biopesticide production, which can directly affect product formulation and consequently product efficiency. However, when it comes to *Bacillus*-based biopesticides production, this downstream separation step has not been addressed comprehensively yet.

Various membrane separation technologies have been used for processing of fermentation broth of various microorganisms [15]. Cross-flow microfiltration has several advantages over conventional technology for separation of cells from extracellular products in bio-industry [13,16,17]. Alongside many advantages over other clarification methods, a serious drawback of microfiltration is membrane fouling, leading to decrease in permeate flux and consequently making microfiltration process uneconomical [18,19]. Membrane fouling is a result of soluble feed components deposition on the membrane surface as well as the buildup of a compressible layer of rejected biomass (i.e., cake layer). Numerous literature data report that the hydraulic resistance associated with cake build-up is the main influencing factor on micro- and/or ultrafiltration in the presence of microbial biomass [20,21]. Furthermore, molecules present in the cultivation broth could also end up bound in the membrane pores, making membrane cleaning even harder and contributing to significant reduction of its life cycle, which is followed by a continuous permeate flux reduction. Therefore, numerous flux enhancement methods have been developed and experimentally investigated in recent years. Physical or chemical feed-mixture pretreatment together with appropriate choice of membrane material could prevent membrane fouling and contribute to increased permeate flux values, as showed in case of microfiltration of *Bacillus thuringiensis* cultivation broth [22,23]. Different flow manipulations could be applied in order to enhance mass transfer near membrane surface, including application of static turbulence promoters [18,24–26] and feed flow alterations, such as pulsing, back-flushing, vibration, etc. [27–30]. Besides increased microfiltration efficiency in terms of permeate flux improvement, reduction of fouling using the aforementioned methods also contributes to membrane life prolongation [31].

Gas sparging during microfiltration assumes introduction of gas into feed mixture flow and achieving two-phase (gas-liquid) flow which is aimed to cause hydrodynamic instabilities in the membrane channel and thus affect concentration polarization in terms of cake layer removal. The main reason for disturbance of cake layer structure is an increase of turbulence shear rate near the membrane surface, which depends on gas and liquid phase linear speed, but also on the gas-liquid flow regime [32]. The presence of gas bubbles in the membrane channel causes efficient removal of loosely bound macromolecules and particles, while breaking of the cake layer could be caused by gas bubbles bursting or coalescence [33,34]. Gas sparging has proven to be efficient in filtration cake removal, hindering of reversible fouling and consequently permeate flux improvement in the studies including filtration of yeast suspension [34–40], titanium oxide suspension [41], skim milk [42], whey [43], *Klebsiella oxytoca* cultivation broth [38], and *Chlorella* sp. suspension [44].

The objective of this study was to assess the efficacy of air sparging as a technique for improvement of permeate flux during microfiltration of *Bacillus velezensis* IP22 cultivation broth, by using response surface methodology for modeling of the microfiltration. Further aim of the study was to maximize permeation flux while simultaneously minimizing

specific energy consumption as a two-objective problem. For the optimization two approaches were analyzed, desirability function method and genetic algorithm.

2. Materials and Methods

2.1. Production of *Bacillus velezensis* Cultivation Broth

Bacillus velezensis IP22, the strain used as an active component of microbial biopesticide, was isolated from fresh cheese and previously identified using 16S rRNA gene sequencing [11]. Preparation of inoculum, i.e., a sufficient amount of a liquid pure culture, was performed by transferring *Bacillus velezensis* IP22 biomass to Erlenmeyer flasks containing sterile liquid medium—nutrient broth (HiMedia, Mumbai, India), followed by cultivation on a laboratory shaker at 28 °C, 150 rpm and under spontaneous aeration for 48 h. The obtained inoculum was used to inoculate the medium in the bioreactor (Biostat® Aplus, Sartorius AG, Göttingen, Germany), while inoculum volume corresponded to 10% (*v/v*) of the bioreactor working volume (2 L). Cultivation medium was previously optimized for production of *Bacillus velezensis* IP22 biopesticide [11,12] and contained glycerol (10 g·L⁻¹), yeast extract (3 g·L⁻¹), (NH₄)₂SO₄ (3 g·L⁻¹), K₂HPO₄ (1 g·L⁻¹), and MgSO₄·7H₂O (0.3 g·L⁻¹), while medium pH value was set to 7.0 ± 0.2. Bioreactor and medium sterilization was performed by autoclaving at 121 °C and 2.1 bar for 20 min. Cultivation of *Bacillus velezensis* IP22 in the bioreactor was carried out at 28 °C, with agitation rate of 250 rpm using Rusthane turbine with three impellers and with aeration rate of 2 L·min⁻¹ using sterile air and ring sparger for gas distribution. The obtained cultivation broth of *Bacillus velezensis* IP22 after 96 h of cultivation in the bioreactor was used as a feed mixture for microfiltration experiments.

In order to assess separation efficiency and viability of *Bacillus velezensis* cells, a standard plate count method was used, where dilutions of the cultivation broth (feed mixture), retentate, and permeate were prepared and used for inoculation of nutrient agar (HiMedia, Mumbai, India). Petri dishes were incubated at 28 °C during 72 h, followed by colony enumeration. Cell concentration was also determined by measuring absorbance (optical density—OD₆₀₀) of the cultivation broth, retentate, and permeate at a wavelength of 600 nm (UV 1800, Shimadzu, Kyoto, Japan). Biomass dry weight determination was performed as follows: biomass pellets obtained after centrifugation of cultivation broth and retentate samples (20 mL) were resuspended using 5 mL of distilled water and dried (105 °C) until reaching a constant weight. Centrifugation was performed at 11,000 rpm for 10 min (Rotina 1080R, Hettich, Kirchleingern, Germany) with sufficient driving force for sedimentation of intact cells, but insufficient for sedimentation of cell debris. The concentration of *Bacillus velezensis* (g·L⁻¹) was calculated using biomass dry weight and the volume of cultivation broth, retentate, or permeate sample (20 mL) which was centrifuged.

2.2. Microfiltration Experimental Setup

Experiments of *Bacillus velezensis* IP22 cultivation broth microfiltration were conducted using the previously described apparatus [25]. All microfiltration experiments were performed at 25 °C and with recirculation of retentate and permeate to maintain a constant volume of the feed mixture. The applied ceramic membrane (Tami Deutschland, Hermsdorf, Germany) had the following characteristics: length 250 mm, inner diameter 6 mm, outer diameter 10 mm, pore size 200 nm, and specific surface area 0.00433 m² (designated as A in the Equations (1) and (2)). The pressurized air was introduced into the feed flow channel through the three-way valve without the diffuser. The air flow rate was measured by the mass flow controller type EL-FLOW F-201AV, with an accuracy of ±0.5% (Bronkhorst, Ruurlo, Netherlands). During microfiltration, the time (*t*) necessary to collect 20 mL (*V*) of permeate was measured and permeate flux value (*J*, L·m⁻²·h⁻¹) was calculated using the Equation (1):

$$J = \frac{V}{A \cdot t} \quad (1)$$

Specific energy consumption per m³ of permeate (E , kW·h·m⁻³) is equal to the ratio of sum of hydraulic and pneumatic powers to the permeate flow rate and it was calculated according to Equation (2):

$$E = \frac{Q_L \cdot (P_S - P_D) + \frac{\gamma}{\gamma-1} \cdot P_D \cdot Q_{G,D} \cdot \left[\left(\frac{P_S}{P_D} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right]}{J \cdot A} \quad (2)$$

where Q_L (m³·h⁻¹) is feed flow rate, P_S (Pa) is pressure at the beginning of the membrane module, P_D (Pa) is pressure at the end of the membrane module, $Q_{G,D}$ (m³·h⁻¹) is air flow rate at the pressure at the end of the membrane module (P_D), γ is the specific heat ratio for air (1.4), J (m³·m⁻²·h⁻¹) is permeate flux, and A (m²) is the specific membrane area.

2.3. Experimental Data Analysis—Modeling and Optimization

The Box–Behnken's experimental plan (Table 1) with three independent variables (factors) varied at three levels was applied to investigate the effects of transmembrane pressure (TMP: 0.2–1 bar), superficial feed velocity (V_L : 0.43–1.30 m·s⁻¹) and superficial air velocity (V_G : 0.0–0.4 m·s⁻¹) to the following dependent variables (responses): steady state permeate flux (J , L·m⁻²·h⁻¹) and specific energy consumption (E , kW·h·m⁻³). The obtained experimental results were fitted using the second-degree polynomial equation to obtain models for steady state permeate flux and specific energy consumption. The experimental data were analyzed using the factorial ANOVA (analysis of variance). The obtained p -values were used to assess statistical significance of the models' coefficients and both models themselves, while quality of the experimental data fitting was estimated using the Lack-of-fit, Pure error, and R^2 (coefficient of determination) values. The coefficient of determination value can be interpreted as the proportion of variability around the mean for the dependent variable, which can be accounted for by the model. It normally ranges from 0 to 1. Ideally, the value 1 means the perfect fit. A selected second-order polynomial model cannot fit perfectly the measured values, due to measurement errors or relationships between factors and responses that cannot be described by the selected model. Actually, this fact results in deviations of predicted values from the measured ones, i.e., so-called residual values exist at the design points. In the experimental designs, where some runs are replicated, such as the Box–Behnken's experimental plan, ANOVA table will also include a lack-of-fit test. The statistical test based on partitioning the residual error sum of squares into two components: lack-of-fit sum of squares (associated with variation due to factors other than measurement error) and pure error sum of squares (associated with random variation caused by measurement error) is used to assess adequacy of the model. In fact, it is used to describe the functional relationships between the experimental factors and the responses. Low p -value for the lack-of-fit in the ANOVA table means that the analyzed model does not fit the experimental data adequately. All statistical analyses were performed at the significance level of 95% using the Statistica software (v. 13.5, Dell, Round Rock, TX, USA).

The polynomial RSM models are usually used for the optimization by the desirability function approach [45]. One of many engineering optimization techniques is multi-objective genetic algorithm (GA) that represents a guided random search method. It is suitable for solving multi-objective optimization problems, capable of exploring the diverse regions of the solution space. The multi-objective optimization by the GA was performed by a non-dominated sorting genetic algorithm II (NSGA-II) [46], which generates a set of non-dominated Pareto optimal solutions. The plot of the Pareto front was drawn between the two objective functions: steady-state permeate flux (J) and specific energy

consumption (E). The optimization problem studied is represented mathematically by Equation (3):

$$\begin{aligned} & \max J(TMP, V_L, V_G), \min E(TMP, V_L, V_G) \\ & \text{subject to bound constraints} \begin{cases} 0.2 \text{ bar} \leq TMP \leq 1 \text{ bar} \\ 0.43 \text{ m}\cdot\text{s}^{-1} \leq V_L \leq 1.30 \text{ m}\cdot\text{s}^{-1} \\ 0.0 \text{ m}\cdot\text{s}^{-1} \leq V_G \leq 0.4 \text{ m}\cdot\text{s}^{-1} \end{cases} \end{aligned} \quad (3)$$

Table 1. Box–Behnken’s experimental plan for *Bacillus velezensis* IP22 cultivation broth microfiltration experiments with air sparging—factors and responses.

Experiment	Factors—Independent Variables			Responses—Dependent Variables	
	TMP (bar)	V_L (m·s ^{−1})	V_G (m·s ^{−1})	J (L·m ^{−2} ·h ^{−1})	E (kW·h·m ^{−3})
1	0.2 (−1)	0.43 (−1)	0.2 (0)	31.06	1.1
2	1.0 (1)	0.43 (−1)	0.2 (0)	22.95	2.3
3	0.2 (−1)	1.30 (1)	0.2 (0)	55.89	4.4
4	1.0 (1)	1.30 (1)	0.2 (0)	70.00	3.9
5	0.2 (−1)	0.87 (0)	0.0 (−1)	30.57	2.4
6	1.0 (1)	0.87 (0)	0.0 (−1)	29.00	4.7
7	0.2 (−1)	0.87 (0)	0.4 (1)	36.67	3.8
8	1.0 (1)	0.87 (0)	0.4 (1)	41.47	2.5
9	0.6 (0)	0.43 (−1)	0.0 (−1)	17.50	2.3
10	0.6 (0)	1.30 (1)	0.0 (−1)	53.87	4.0
11	0.6 (0)	0.43 (−1)	0.4 (1)	32.64	1.1
12	0.6 (0)	1.30 (1)	0.4 (1)	58.05	4.6
13	0.6 (0)	0.87 (0)	0.2 (0)	43.45	2.1
14	0.6 (0)	0.87 (0)	0.2 (0)	42.80	2.1
15	0.6 (0)	0.87 (0)	0.2 (0)	45.00	2.0

TMP—transmembrane pressure, V_L —superficial feed velocity, V_G —superficial air velocity, J—steady state permeate flux, E—specific energy consumption.

The Design-Expert software v. 8.1 (Stat-Ease, Inc., Minneapolis, MN, USA) was used for generating the polynomial RSM models and optimization by the desirability function approach, while for the GA optimization Matlab software (R2015b, MathWorks, Natick, MA, USA) was used.

3. Results

3.1. Modeling of Gas Sparging-Assisted Microfiltration of *Bacillus velezensis* IP22 Cultivation Broth

Microfiltration experiments were performed according to the Box–Behnken’s experimental plan (Table 1), where the effects of microfiltration operational conditions (transmembrane pressure, TMP— X_1 , superficial feed velocity, V_L — X_2 , and superficial air velocity, V_G — X_3) to steady state permeate flux (J) and specific energy consumption (E) were investigated. Combinations of experimental factors (actual values of variables and coded values of variables in parentheses) and values of responses are summarized in Table 1. As the Box–Behnken’s experimental plan was defined for three independent variables varied at three levels, the coded values of independent variables represent the equally distant varied levels of the independent variables’ values (−1, 0, and 1).

The obtained experimental data were fitted using the second-degree polynomial equation to obtain models describing the effects of the aforementioned operational parameters to microfiltration performance. The linear (b_1, b_2, b_3), quadratic (b_{11}, b_{22}, b_{33}), and interaction (b_{12}, b_{13}, b_{23}) model coefficients in terms of coded and actual variables’ values and the corresponding p -values are given in Table 2. Statistical significant coefficients, with p -values less than 0.05, are bolded in Table 2. The presented results have indicated statistical significance of linear effects of superficial feed velocity and superficial air velocity, quadratic effects of each independent variable and interaction effects of transmembrane

pressure and superficial feed velocity, as well as superficial feed velocity and superficial air velocity, to steady state permeate flux. On the other hand, statistical significance for specific energy consumption was observed for the same effects as in the case of steady state permeate flux, with additional statistical significant effect of interaction between transmembrane pressure and superficial air velocity (Table 2).

Table 2. Coefficients of regression models for steady state permeate flux and specific energy consumption for microfiltration of *Bacillus velezensis* IP22 cultivation broth aided with air sparging.

Effects	Steady State Permeate Flux (L·m ⁻² ·h ⁻¹)			Specific Energy Consumption (kW·h·m ⁻³)		
	Coefficient Actual	Coefficient Coded	<i>p</i> -Value	Coefficient Actual	Coefficient Coded	<i>p</i> -Value
Intercept						
<i>b</i> ₀	20.25	43.56	0.0141	0.78	2.05	0.0302
Linear						
<i>b</i> ₁	−10.54	1.12	0.1410	0.37	0.21	0.0009
<i>b</i> ₂	−9.62	16.71	<0.0001	0.88	1.26	<0.0001
<i>b</i> ₃	107.98	4.75	0.0007	−5.40	−0.18	0.0021
Quadratic						
<i>b</i> ₁₁	−15.20	−2.43	0.0017	3.78	0.60	0.0002
<i>b</i> ₂₂	20.34	3.85	0.0096	1.42	0.27	<0.0001
<i>b</i> ₃₃	−172.28	−6.89	0.0295	16.98	0.68	0.0001
Interaction						
<i>b</i> ₁₂	31.90	5.55	0.0499	−2.45	−0.42	<0.0001
<i>b</i> ₁₃	19.91	1.59	0.1400	−11.25	−0.90	0.0018
<i>b</i> ₂₃	−31.51	−2.74	0.0008	5.17	0.45	<0.0001

ANOVA (analysis of variance) was performed to assess statistical significance of the obtained models for steady state permeate flux and specific energy consumption (Table 3). Based on the presented results, it could be concluded that the both second-degree mathematical models were statistically significant (with *p*-values less than 0.05, bolded in Table 3) and adequate in terms of quality of the experimental results fitting, with values of determination coefficient (*R*²) over 0.9. The ANOVA as given in Table 3 showed that coefficient of determination was 0.984 and 0.995, for second-degree polynomial models for permeate flux and specific energy consumption, respectively. That means that the permeate flux model could explain 98.4% of the variation in response, while in the case of specific energy consumption, the value is 99.5%, which indicated a superb fitness of the models. The high *F* values of the models (95.80 L·m⁻²·h⁻¹ and 318.23 kW·h·m⁻³ for permeate flux and specific energy consumption, respectively), as well as non-significant lack-of-fit (0.22 for permeate flux and 0.26 for specific energy consumption) values showed that models were statistically significant. At the same time, small values of pure error (2.56 for permeate flux and 0.01 for specific energy consumption) indicated that variation caused by measurement error is insignificant. Therefore, these results are indicating that the selected regression model could be used to analyze trends of responses. Second-degree polynomial models could be successfully applied to describe the effects of transmembrane pressure, superficial feed velocity and superficial air velocity to steady state permeate flux and specific energy consumption during microfiltration of *Bacillus velezensis* IP22 cultivation broth aided with air sparging.

Furthermore, response surface plots were generated to better understand interactions of independent variables—operational conditions (transmembrane pressure, superficial feed velocity, and superficial air velocity)—to the selected microfiltration responses—steady-state permeate flux and specific energy consumption. The response surface plots (Figure 1) represent the effects of two independent variables to one response, while the value of the third independent variable was set to the mean value of the examined range of values.

Table 3. ANOVA of regression models for steady state permeate flux and specific energy consumption for microfiltration of *Bacillus velezensis* IP22 cultivation broth aided with air sparging.

Source	Response	DF	SS	MS	F-Value	p-Value	R ²
Model	J (L·m ⁻² ·h ⁻¹)	9	2845.19	316.13	95.80	0.000046	0.984
	E (kW·h·m ⁻³)	9	21.06	2.34	318.23	0.000002	0.995
Residual	J (L·m ⁻² ·h ⁻¹)	5	16.50	3.30			
	E (kW·h·m ⁻³)	5	0.04	0.01			
Lack-of-fit	J (L·m ⁻² ·h ⁻¹)	3	13.94	4.65	3.64	0.22	
	E (kW·h·m ⁻³)	3	0.03	0.01	3.01	0.26	
Pure error	J (L·m ⁻² ·h ⁻¹)	2	2.56	1.28			
	E (kW·h·m ⁻³)	2	0.01	0.00			
Total	J (L·m ⁻² ·h ⁻¹)	14	2861.68				
	E (kW·h·m ⁻³)	14	21.10				

J—steady state permeate flux, E—specific energy consumption, DF—degree of freedom, SS—sum of squares, MS—mean squares, R²—coefficient of determination.

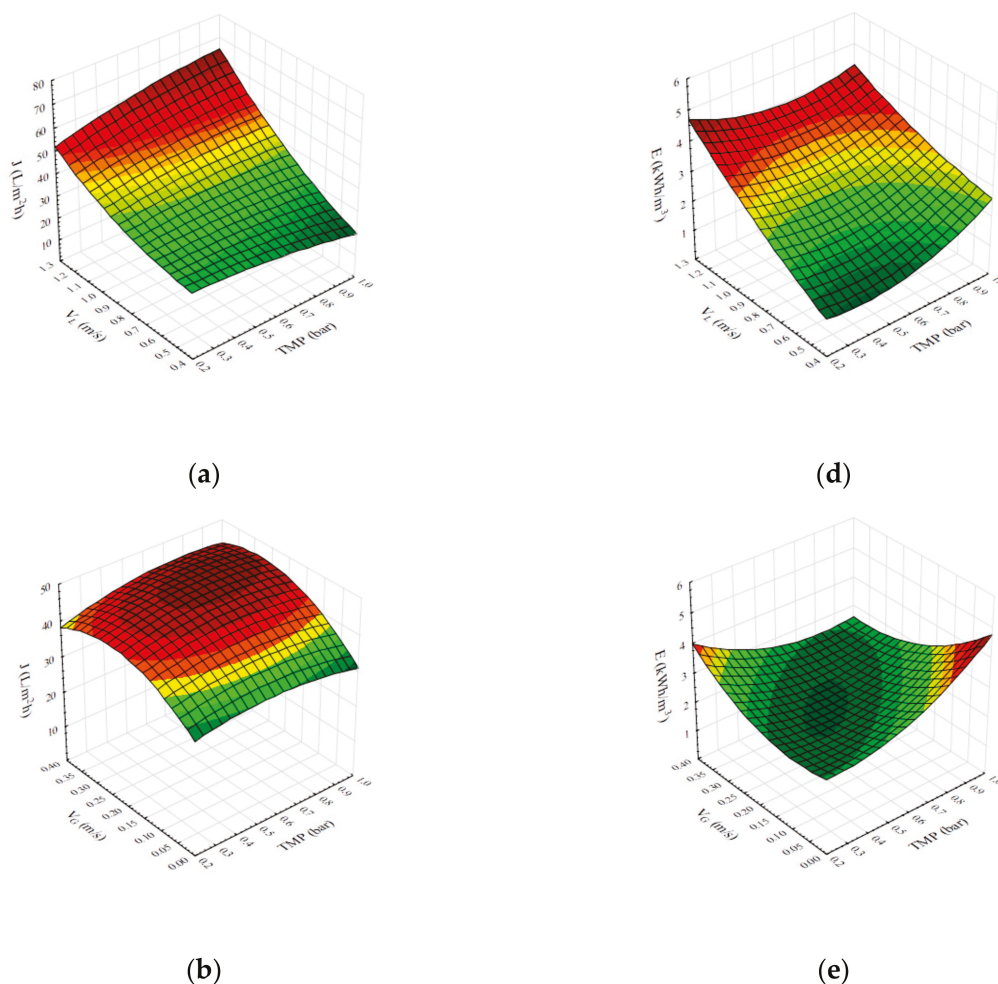


Figure 1. Cont.

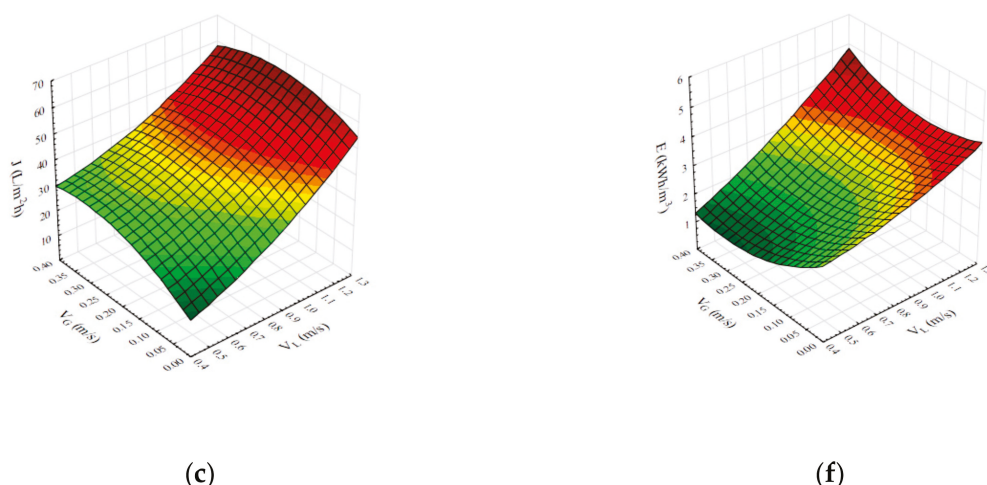


Figure 1. Response surface plots representing the regression models for steady state permeate flux (a–c) and specific energy consumption (b–d) during microfiltration of *Bacillus velezensis* IP22 cultivation broth aided with air sparging. The response surface plots represent the following effects of the independent variables to the aforementioned responses: (a) transmembrane pressure (TMP) and superficial feed velocity (V_L) to permeate flux (J); (b) transmembrane pressure (TMP) and superficial air velocity (V_G) to permeate flux (J); (c) superficial feed velocity (V_L) and superficial air velocity (V_G) to permeate flux (J); (d) transmembrane pressure (TMP) and superficial feed velocity (V_L) to specific energy consumption (E); (e) transmembrane pressure (TMP) and superficial air velocity (V_G) to specific energy consumption (E); (f) superficial feed velocity (V_L) and superficial air velocity (V_G) to specific energy consumption (E).

As can be seen in Figure 1a, high values of steady-state permeate flux were obtained at the highest applied values of superficial feed velocity across the whole range of transmembrane pressure values, with the highest value of permeate flux obtained at the highest value of transmembrane pressure applied. A similar effect could be observed when it comes to interaction of transmembrane pressure and superficial air velocity, with slight decrease of permeate flux at the highest value of superficial air velocity (Figure 1b). Furthermore, interaction of superficial feed velocity and superficial air velocity has showed that the highest value of steady state permeate flux was achieved at the highest value of superficial feed velocity across the whole range of superficial air velocity values (Figure 1c).

On the other hand, the increase of specific energy consumption could be observed with the increase of superficial feed velocity, while the lowest value of specific energy consumption was obtained at the lowest value of transmembrane pressure (Figure 1d). The lowest value of specific energy consumption was achieved by applying middle range values of transmembrane pressure and superficial air velocity (Figure 1e). Interaction of superficial feed velocity and superficial air velocity has resulted in the lowest value of specific energy consumption at the lowest value of superficial feed velocity and the highest value of superficial air velocity (Figure 1f).

The analyses of cell viability and concentration have showed that *Bacillus velezensis* cells have been completely retained by the membrane. Biomass concentration of *Bacillus velezensis* in the fresh cultivation broth was 0.39 g·L⁻¹, while after the filtration experiments biomass concentration in the retentate was 0.36 g·L⁻¹. Spectrophotometric measurements (OD₆₀₀) also confirmed this fact, and the absorbance values were 0.82 for the fresh cultivation broth and 0.77 for the retentate sample after microfiltration experiments. The results of the standard plate count method correspondingly suggested that the cells retained by the membrane did not suffer either significant change in the cell concentration nor decrease in the cell viability due to shear disintegration by pumping or mixer effects.

3.2. Optimization of Gas Sparging-Assisted Microfiltration of *Bacillus velezensis* IP22 Cultivation Broth

Optimization of operational conditions during air sparging-assisted microfiltration of *Bacillus velezensis* IP22 cultivation broth was performed using the desirability function approach. Optimization was aimed at maximizing steady state permeate flux and minimizing specific energy consumption. This method combines multiple responses into one response called the desirability function. The selected responses are transformed to an individual desirability values in range from 0 to 1. The overall desirability of the process is computed as a geometric mean of the individual desirability functions [24]. From the optimization results of the desirability function approach (Table 4) it can be concluded that the optimal results in terms of steady state permeate flux and specific energy consumption were obtained at transmembrane pressure value of 0.68 bar, superficial feed velocity of $0.96 \text{ m}\cdot\text{s}^{-1}$ and superficial air velocity of $0.25 \text{ m}\cdot\text{s}^{-1}$. The aforementioned optimized values of independent variables would result in predicted values of steady-state permeate flux of $48.57 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and specific energy consumption of $2.37 \text{ kW}\cdot\text{h}\cdot\text{m}^{-3}$. The optimized values of all three independent variables were close to the mean values of the tested range (0.2–1.0 bar for transmembrane pressure, $0.43\text{--}1.30 \text{ m}\cdot\text{s}^{-1}$ for superficial feed velocity, and $0.0\text{--}0.4 \text{ m}\cdot\text{s}^{-1}$ for the superficial air velocity). The obtained value of the desirability function was 0.62 (Table 4).

Table 4. Optimization results obtained by the desirability function approach during microfiltration of *Bacillus velezensis* IP22 cultivation broth aided with air sparging.

Factors—-independent variables	Goal	Optimized value
Transmembrane pressure, TMP (bar)	in range	0.68
Superficial feed velocity, V_L ($\text{m}\cdot\text{s}^{-1}$)	in range	0.96
Superficial air velocity, V_G ($\text{m}\cdot\text{s}^{-1}$)	in range	0.25
Responses—dependent variables	Goal	Predicted value
Steady state permeate flux, J ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$)	maximize	48.57
Specific energy consumption, E ($\text{kW}\cdot\text{h}\cdot\text{m}^{-3}$)	minimize	2.37
Desirability function		0.62

The results of GA optimization are illustrated in Figure 2. The Pareto front reveals the conflicting relationship between steady-state permeate flux and specific energy consumption. The specific energy consumed per cubic meter of the permeate is equal to the ratio of sum of hydraulic and pneumatic powers to the permeate flow rate and is given by Equation (2). It can be reasoned that flux increase due to increased power consumption (both hydraulic and pneumatic) in some cases can result in lower values of specific energy consumption. This is the case when flux increase is sufficiently high to lower the ratio of energy consumption to permeate flux, given by Equation (2). The optimized values of transmembrane pressure had a distribution between 0.4 bar and 1.0 bar. Optimized value range of superficial feed velocity expanded on the whole range of the investigated experimental values, while on the other side, optimized value of superficial air velocity had a narrow distribution around $0.25 \text{ m}\cdot\text{s}^{-1}$. As for the objective functions, their ranges were between $1 \text{ kW}\cdot\text{h}\cdot\text{m}^{-3}$ and $4 \text{ kW}\cdot\text{h}\cdot\text{m}^{-3}$ for specific energy consumption, and between $33 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and $70 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ for steady-state permeate flux.

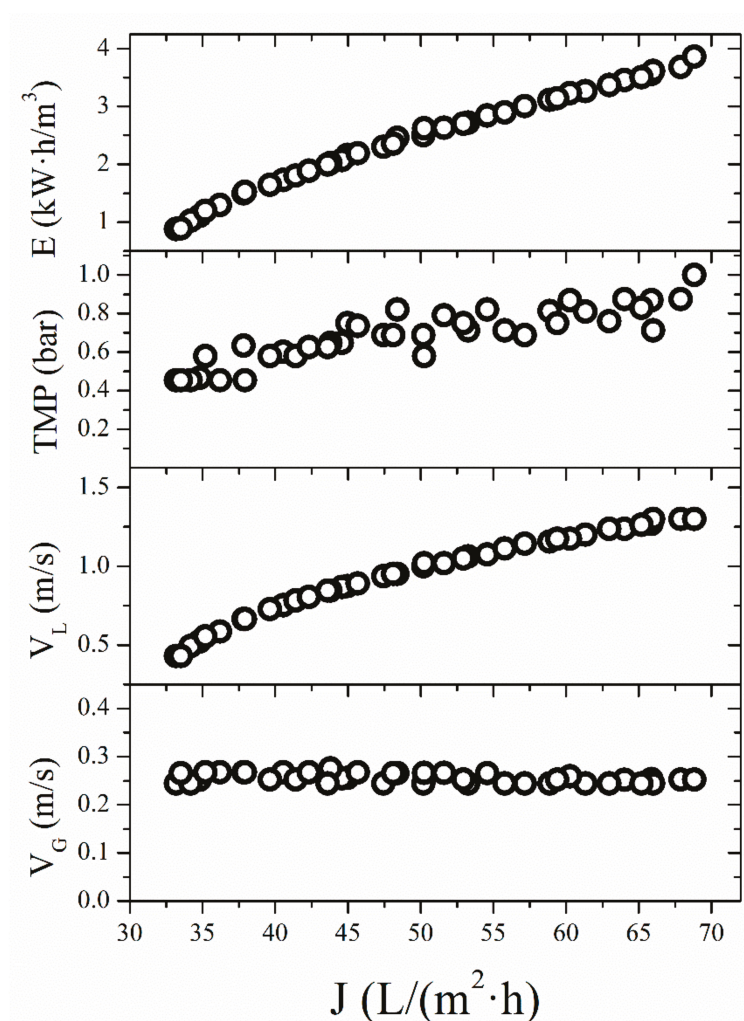


Figure 2. The Pareto front plot and decision space of the optimal solution set obtained from the multi-objective genetic algorithm optimization during microfiltration of *Bacillus velezensis* IP22 cultivation broth aided with air sparging.

4. Discussion

4.1. The Effects of Operational Conditions on Steady State Permeate Flux during Air Sparging-Assisted Microfiltration of *Bacillus velezensis* IP22 Cultivation Broth

As it was previously stated, the obtained second-degree models for steady-state permeate flux and specific energy consumption during microfiltration of *Bacillus velezensis* IP22 cultivation broth aided with air sparging have proven to be statistically significant and appropriate for fitting of the obtained microfiltration experimental data. Furthermore, response surface plots were generated to better understand interactions of operational conditions (transmembrane pressure, superficial feed velocity, and superficial air velocity) to the selected responses (Figure 1).

The increase in steady-state permeate flux values was observed with the increase of superficial feed velocity value for all values of transmembrane pressure in the examined range (Figure 1a). Maximal permeate flux values are achieved in the region of the higher feed velocity values although this region corresponds to bubbly flow pattern, which is commonly associated with lower flux augmentations in the literature [33,36,47]. For the superficial feed velocity values of 0.43, 0.86, and 1.30 m·s^{−1}, the corresponding Reynolds' number values are 1990, 3980, and 5971, respectively. Therefore, at the higher values of feed velocity turbulent flow exists even without gas sparging. The filtration cake thickness has reduced by increasing the superficial feed velocity, so the cake resistance to the flux flow was smaller and consequently the permeate flux value was higher. Due to

the variation of bacterial cell arrangement in the cake layer, the permeate flux increase at the lower values of transmembrane pressure is less significant compared to the higher values of transmembrane pressure [48]. As superficial feed velocity increased from 0.43 to $1.30 \text{ m}\cdot\text{s}^{-1}$, the permeation flux increased $\sim 180\%$ at the transmembrane pressure of 1 bar, while the increase of $\sim 67\%$ was observed in the same range of superficial feed velocity at the transmembrane pressure of 0.2 bar (Figure 1a). From the beginning of microfiltration at higher values of transmembrane pressure, the cells deposit randomly, as the cake formation is dominated by the permeation flow perpendicular to the membrane surface. On the other hand, with microfiltration progression permeation flux decreases, so the bacterial cells are arranged by the feed flow parallel to the membrane surface. The increase in superficial feed velocity results in cake thickness reduction, so the cell layer arranged by the feed flow is carried away, resulting in the reduced cake resistance, i.e., the influence of increase in superficial feed velocity is more pronounced at higher values of transmembrane pressure. Conversely, when lower values of transmembrane pressure are applied, the bacterial cell layer arrangement by the feed flow occurs earlier in the microfiltration process due to the low permeation fluxes [27,48], so at steady state, the increase of superficial feed velocity is not as effective in reducing cake resistance as for the higher values of transmembrane pressure. The influence of increase in transmembrane pressure on the steady state permeate flux is less manifested and to some extent ambiguous (puzzling) (Figure 1a). At the higher values of superficial feed velocity, increase of transmembrane pressure results in a moderate increase of steady state flux—approximately 24% . Increase of superficial feed velocity in membrane channel creates turbulence, which reduces the cake layer resistance by changing the fluid flow field and by increasing particle back transport through turbulent diffusion [49]. On the other hand, reduction in steady state permeate flux ($\sim 38\%$) with the increase of transmembrane pressure is observed at the lower values of superficial feed velocity (Figure 1a). The justification for this occurrence could be found in the shear-induced arrangement of *Bacillus velezensis* rod-shaped cells, that results in formation of the brick-like structure at the cake surface [20,50]. In the literature, similar results are reported for cross-flow microfiltration of other rod-like particles such as graphene oxide [16] or microorganisms with rod-shaped cells: *Pseudomonas* sp. [51], *Bacillus coagulans* [20], and *Escherichia coli* [52]. It seems that in the region of lower feed velocity values, turbulence caused by both air and feed flows is not sufficient to increase the steady state permeate flux by increasing transmembrane pressure. On the other hand, it is reported that air sparging might compress filtration cake to a more compact structure [33,34,40], so the cake resistance is higher as the cake is compacted more by raising transmembrane pressure and thus permeate flux value declines.

The effects of transmembrane pressure and superficial air velocity on the steady state permeate flux are given in Figure 1b. Increase of superficial air velocity up to the range of $0.25 \text{ m}\cdot\text{s}^{-1}$ to $0.30 \text{ m}\cdot\text{s}^{-1}$ resulted in increase of permeate flux at all transmembrane pressure values. However, further increase of superficial air velocity led to a modest permeate flux decline at lower values of transmembrane pressure. Similar results have been reported for air sparged microfiltration of yeast [34] and clay suspension [32]. In the case of clay suspension, it is stated that the maximal permeate flux was obtained at higher values of superficial air velocity indicating that filtration cake properties are greatly affected by the air sparging [32]. The influence of increase in superficial air velocity is more obvious at the higher values of transmembrane pressure because the membrane fouling was more severe compared to the lower values of transmembrane pressure. Similar results were reported for whey air sparging-assisted microfiltration [43]. As superficial air velocity value increased from 0.00 to $0.40 \text{ m}\cdot\text{s}^{-1}$, the permeation flux has risen for around 45% at 1.0 bar, while its increase of $\sim 23\%$ has been observed in the same range of superficial air velocity values under transmembrane pressure of 0.2 bar (Figure 1b). As previously noted, another reason for this behavior can be found in the fact that air sparging might compress filtration cake to a more compact structure [40]. Hwang and Hsu [34] reported that during yeast air sparged microfiltration the cake properties were

mainly determined by the yeast cells. The influence of cell shape on the cake structure is even more prominent for *Bacillus velezensis* rod-shaped cells compared to the oval yeast cells, as they tend to orientate parallel to feed flow [48,50]. In addition, an increase in filtration pressure leads to formation of cake with the higher resistance, so no influence of transmembrane pressure on the permeate flux was noted in the situation without air sparging. On the other hand, in the region of the highest values of superficial air velocity (the highest turbulence), ~14% increase in permeate flux value was achieved with an increase of transmembrane pressure (Figure 1b). As Figure 1b was drawn for the third factor (superficial feed velocity) set to its medium value (0.86 m/s) from the examined range, it is reasonable to assume that the higher values of superficial feed velocity would result in moderate rise of permeate flux with an increase of the transmembrane pressure due to improved turbulence in the membrane channel.

Figure 1c shows the simultaneous influence of superficial feed and air velocities on the steady state permeate flux. Increase of superficial air velocity value up to $0.40 \text{ m}\cdot\text{s}^{-1}$ at the higher values of superficial feed velocity ($1.30 \text{ m}\cdot\text{s}^{-1}$) did not show significant effect to permeate flux, as the flux value has risen for ~6%. Substantial flux improvement was not achieved in these operational conditions as the high superficial feed velocity corresponds to turbulent regime (Reynolds' number above 5900). Therefore, the air injection was not efficient enough to make the flow more turbulent [43]. On the other hand, in the lower value range of superficial feed velocity, increase of superficial air velocity resulted in larger increase of permeate flux. For example, at superficial feed velocity of $0.43 \text{ m}\cdot\text{s}^{-1}$ increase of superficial air velocity up to $0.40 \text{ m}\cdot\text{s}^{-1}$ resulted in increase of permeate flux value of 78% in the slug gas–liquid flow regime (Figure 1c). As reported in the literature, slug flow pattern induces enough turbulence to hinder cake formation [33,36,43,47]. At low values of superficial feed velocity ($0.43 \text{ m}\cdot\text{s}^{-1}$), a plateau in permeate flux values was observed during increase of superficial air velocity values from $0.25 \text{ m}\cdot\text{s}^{-1}$ to $0.40 \text{ m}\cdot\text{s}^{-1}$. This plateau became shorter with the increasing value of superficial feed velocity, while for the highest values of superficial feed and air velocities a decrease in permeate flux was observed. Air sparging reduces external membrane fouling by reducing filtration cake. The cake acts as a self-rejective dynamic membrane and protects membrane from internal fouling. Synergistic effect of both superficial feed and air velocities can cause the cake layer to become too thin and allow smaller components of the cultivation broth to penetrate into the membrane pores and thus reduce permeation flux [47]. Predictably, without air sparging, the permeate flux increased with the increase of superficial feed velocity as the higher wall shear stress reduced the cake formation. Nevertheless, the permeate flux improvement achieved by increasing superficial feed velocity is less significant combined with the higher values of superficial air velocity due to the increased level of turbulence. In the situation without air sparging, when superficial feed velocity value increased from $0.43 \text{ m}\cdot\text{s}^{-1}$ to $1.30 \text{ m}\cdot\text{s}^{-1}$, the permeation flux value rose for 200%, while it increased for ~80% in the same value range of superficial feed velocity, but under air sparging with superficial air velocity of $0.40 \text{ m}\cdot\text{s}^{-1}$.

The results of air sparged microfiltration of the *Bacillus velezensis* IP22 cultivation broth suggest that significant steady state permeate flux improvements could be achieved by applying two-phase flow. The increase in permeate flux is a result of not only an increase in superficial feed velocity by the two-phase flow, but also by the air flow itself, which creates instabilities in the feed flow [36]. This fact is proven by comparing the permeate flux values for the experiments with and without air sparging by selecting values of superficial air and feed velocities to be adjusted to levy the same mean velocity in the membrane channel. In the experiment without air sparging (TMP = 0.6 bar, $V_L = 0.60 \text{ m}\cdot\text{s}^{-1}$ and $V_G = 0.00 \text{ m}\cdot\text{s}^{-1}$) steady-state permeate flux value was $21.5 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$. On the other hand, in the experiment with the two-phase flow (TMP = 0.6 bar, $V_L = 0.43 \text{ m}\cdot\text{s}^{-1}$ and $V_G = 0.18 \text{ m}\cdot\text{s}^{-1}$) the permeate flux value was $29.4 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, which represents an increase of 37%. From the economic point of view, investigation of specific energy consumption is necessary for the selection of the appropriate operational

conditions. In the case of these two experiments, specific energy consumption values were $1.2 \text{ kW}\cdot\text{h}\cdot\text{m}^{-3}$ and $2.5 \text{ kW}\cdot\text{h}\cdot\text{m}^{-3}$ for the experiments with and without air sparging, respectively, suggesting that introduction of air into the membrane channel reduced specific energy consumption by 108%.

4.2. The Effects of Operational Conditions on Specific Energy Consumption during Air Sparging-Assisted Microfiltration of *Bacillus velezensis* Cultivation Broth

The efficiency of air sparging during microfiltration of *Bacillus velezensis* IP22 cultivation broth was also determined by investigating specific energy consumption as the energy dissipated per permeate volume unit. The influences of microfiltration operational conditions on the specific energy consumption are given in Figure 1.

The increase in specific energy consumption is observed with the increase of superficial feed velocity for the whole value range of transmembrane pressure (Figure 1d). As the pumping energy is directly proportional to the feed flow rate, an increase in superficial feed velocity results in higher energy consumption. On the other hand, the increase of permeate flux in this regime was not high enough to compensate increased energy demand as the specific energy consumption is related to the permeate flow. As the increase of permeate flux was more pronounced for the higher values of transmembrane pressure (Figure 1a), consequently energy consumption per permeate volume unit was moderately rising (74%) for these experimental conditions compared to the rise of 300% at lower values of transmembrane pressure (i.e., 0.2 bar). At the higher values of superficial feed velocity, increase in transmembrane pressure resulted in permeate flux increase, so the specific energy consumption decreased for 10% in the selected experimental range. On the other side, *Bacillus velezensis* cell orientation in combination with increase of transmembrane pressure results in filtration cake with higher resistance [20,50]. Therefore, for lower permeate flux values energy consumption per permeate volume unit increased for ~130%, from $1.0 \text{ kW}\cdot\text{h}\cdot\text{m}^{-3}$ to $2.3 \text{ kW}\cdot\text{h}\cdot\text{m}^{-3}$.

The effects of transmembrane pressure and superficial air velocity on the specific energy consumption are given in Figure 1e. The concave surface shape indicates that minimal values of the specific energy consumption (approximately $2.0 \text{ kW}\cdot\text{h}\cdot\text{m}^{-3}$) were recorded for median values of transmembrane pressure and superficial air velocity. Increase of superficial air velocity up to a range of $0.20 \text{ m}\cdot\text{s}^{-1}$ to $0.30 \text{ m}\cdot\text{s}^{-1}$ resulted in minor decrease of specific energy consumption at lower (0.2 bar) and median (0.7 bar) values of transmembrane pressure, respectively. Further increase of superficial air velocity caused incline of the specific energy consumption for the aforementioned value range of transmembrane pressure. The steepest increase (58%) in specific energy consumption was recorded at transmembrane pressure of 0.2 bar. However, at transmembrane pressure values higher than 0.7 bar, the trend of specific energy consumption decline remained for the full value range of superficial air velocity. The steepest decline (84%) of the specific energy consumption was recorded at transmembrane pressure of 1.0 bar (Figure 1e). Improved turbulence by applying higher value of superficial air velocity ($0.40 \text{ m}\cdot\text{s}^{-1}$) resulted in specific energy demand decrease by 52% for transmembrane pressure value rise from 0.2 to 1.0 bar (Figure 1e). In contrast, in the case without gas sparging specific energy consumption has risen 92% with increase of transmembrane pressure. At these experimental conditions, without air sparging or at low values of superficial air velocity, the increase of transmembrane pressure did not result in permeate flux increase. The reason for this is probably marginal influence of air bubbles on filtration cake that compacts with an increase of filtration pressure [44]. The increase is due to the fact that to reach higher values of transmembrane pressure, a higher value of feed pressure is needed, thus the insignificant change of flux results in higher specific energy consumption.

Figure 1f shows the simultaneous influence of superficial feed and air velocities on the specific energy consumption. Specific energy consumption increased with the increase of superficial feed velocity across the whole value range of superficial air velocity, by means of energy input of feed pumping. Due to the significant increase of permeate flux without air sparging with increased value of superficial feed velocity, the rise of

specific energy consumption was hindered, and it was ~66%. For maximal values of superficial air velocity, this increase was steeper (310%)—from $1.1 \text{ kW}\cdot\text{h}\cdot\text{m}^{-3}$ to $4.5 \text{ kW}\cdot\text{h}\cdot\text{m}^{-3}$. In contrast to the influence of superficial feed velocity, increase of superficial air velocity value up to $\sim 0.25 \text{ m}\cdot\text{s}^{-1}$ resulted in reduction of specific energy consumption from $2.4 \text{ kW}\cdot\text{h}\cdot\text{m}^{-3}$ to $1.1 \text{ kW}\cdot\text{h}\cdot\text{m}^{-3}$, i.e., 120%. For further increase in superficial air velocity, there were no significant changes in specific energy consumption at lower values of superficial feed velocity. On the other hand, for higher values of superficial feed velocity ($1.30 \text{ m}\cdot\text{s}^{-1}$) increase of superficial air velocity over $0.25 \text{ m}\cdot\text{s}^{-1}$ resulted in slight increase of 12.5% in energy consumption per permeate volume unit. This behavior can be explained by the membrane internal fouling triggered by a significant cake reduction in the area of high values of both feed and air velocities.

4.3. Optimization of Operational Conditions for Air Sparging-Assisted Microfiltration of *Bacillus velezensis* Cultivation Broth

Optimization of the operational parameters during microfiltration of *Bacillus velezensis* IP22 cultivation broth was performed using two approaches: desirability function method and genetic algorithm. The optimization was aimed at maximization of steady state permeate flux and minimization of specific energy consumption, in order to achieve maximal efficiency and cost effectiveness of microfiltration as the downstream operation in production of *Bacillus velezensis*-based biopesticide. When it comes to the optimization results, it could be concluded that there exists an opposite nature of the optimization goals, i.e., the antagonistic relationship of the examined dependent variables—steady-state permeate flux and specific energy consumption. The optimized value of superficial air velocity correlates with the results obtained by applying the response surface methodology. When it comes to superficial feed velocity and transmembrane pressure, the optimized values of these two independent variables were closer to the maximal values of the tested ranges as these values favor the maximization of permeate flux, but also result in an increase in specific energy consumption. Therefore, the satisfactory optimization solution by the desirability function approach (with desirability function value of 0.62) was achieved with the optimized values of independent variables that are close to the mean values of the examined value ranges (Table 4).

The optimum prediction by the desirability function approach is in agreement with the Pareto front. Even though the Pareto front offers many optimal solutions, the problem of choosing a compromise solution still exists. Suitable solution can be selected by taking into account the desired optimization goal(s), but trade-offs among different objectives are necessary [53]. If the optimization goal was set at maximal value of steady-state permeate flux, higher values of superficial feed velocity should be applied, as well as higher values of transmembrane pressure. In this case, specific energy consumption value was higher. By contrast, when the goal was to achieve lower values of specific energy consumption, lower values of superficial feed velocity should be used. When it comes to superficial air velocity, in all optimal solutions given by the Pareto front (Figure 2) optimized values were around $0.25 \text{ m}\cdot\text{s}^{-1}$.

5. Conclusions

This study was aimed at investigating the effect of air sparging as a technique to achieve higher microfiltration efficiency when it comes to separation of *Bacillus velezensis* IP22 biomass aimed to be used as microbial biopesticide, as well as at modeling and optimization of the microfiltration process. The obtained second-degree polynomial models for dependent variables (steady-state permeate flux and specific energy consumption) have proven to be statistically significant and appropriate for fitting of the microfiltration experimental data. Application of the response surface methodology approach for microfiltration modeling has revealed significant effects of interactions between the main microfiltration parameters (transmembrane pressure, superficial feed velocity, and superficial air velocity) to the selected responses. Optimization was performed using the desirability function method and genetic algorithm, and it was aimed at maximization of

steady-state permeate flux and minimization of specific energy consumption, as a two-objective problem. Both methods have revealed antagonistic relationship between the selected responses, while the optimal results of the operational parameters were set near median values of the investigated value ranges. The results of this study have confirmed a significant potential of air sparging to be used as a technique of choice for improvement of microfiltration efficiency and cost effectiveness. With improvement of permeate flux as a result, application of this technique primarily results in reduced membrane fouling, which also cuts down the membrane cleaning frequency and consequently increases the microfiltration operational time between the cleanings. In this way, membrane life cycle is also prolonged, which directly affects overall downstream cost, together with reduction of energy consumption during microfiltration. Considering high costs of biotechnological production of microbial biopesticides and high share of downstream processing in the overall bioprocess cost, air sparging-assisted microfiltration should be further examined as a downstream operation for not only production of microbial biopesticides, but also for downstream processing of other bacterial cultivation broths.

Author Contributions: Conceptualization, A.J. and I.P.; methodology, J.G. and I.P.; software, N.L. and A.K.; validation, A.J., I.P., and J.G.; formal analysis, S.D. and V.V.; investigation, I.P., V.V., and S.D.; resources, A.J., J.G., and N.L.; data curation, A.K. and N.L.; writing—original draft preparation, A.J. and I.P.; writing—review and editing, A.J., I.P., and J.G.; visualization, N.L.; supervision, I.P.; project administration, J.G.; funding acquisition, A.J., N.L., A.K., S.D., and J.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia, grant number 451-03-68/2021-14/200134.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

References

1. Cidón, C.F.; Figueiró, P.S.; Schreiber, D. Benefits of organic agriculture under the perspective of the bioeconomy: A systematic review. *Sustainability* **2021**, *13*, 6852. [CrossRef]
2. Seiber, J.N.; Coats, J.; Duke, S.O.; Gross, A.D. Biopesticides: State of the art and future opportunities. *J. Agric. Food Chem.* **2014**, *62*, 11613–11619. [CrossRef]
3. Rui, L. Microbial biopesticides in agroecosystems. *Agronomy* **2018**, *8*, 235. [CrossRef]
4. Reganold, J.; Wachter, J. Organic agriculture in the twenty-first century. *Nat. Plants* **2016**, *2*, 15221. [CrossRef]
5. Muller, A.; Schader, C.; El-Hage Scialabba, N.; Brüggemann, J.; Isensee, A.; Erb, K.; Smith, P.; Klocke, P.; Leiber, F.; Stolze, M.; et al. Strategies for feeding the world more sustainably with organic agriculture. *Nat. Commun.* **2017**, *8*, 1290. [CrossRef]
6. Shafi, J.; Tian, H.; Ji, M. *Bacillus* species as versatile weapons for plant pathogens: A review. *Biotechnol. Biotechnol. Equip.* **2017**, *31*, 446–459. [CrossRef]
7. Fira, D.; Dimkić, I.; Berić, T.; Lozo, J.; Stanković, S. Biological control of plant pathogens by *Bacillus* species. *J. Biotechnol.* **2018**, *285*, 44–55. [CrossRef]
8. Villarreal-Delgado, M.F.; Villa-Rodríguez, E.D.; Cira-Chávez, L.A.; Estrada-Alvarado, M.I.; Parra-Cota, F.I.; de los Santos-Villalobos, S. The genus *Bacillus* as a biological control agent and its implications in the agricultural biosecurity. *Rev. Mex. Fitopatol.* **2018**, *36*, 95–130. [CrossRef]
9. Rabbee, M.F.; Ali, M.S.; Choi, J.; Hwang, B.S.; Jeong, S.C.; Baek, K.-h. *Bacillus velezensis*: A valuable member of bioactive molecules within plant microbiomes. *Molecules* **2019**, *24*, 1046. [CrossRef]
10. Ngali, M.S.; Yahaya, R.S.R.; Baharudin, M.M.A.-a.; Yaminudin, S.M.; Karim, M.; Ahmad, S.A.; Sabri, S. A review on the biotechnological applications of the operational group *Bacillus amyloliquefaciens*. *Microorganisms* **2021**, *9*, 614. [CrossRef] [PubMed]
11. Pajčin, I.; Vlajkov, V.; Frohme, M.; Grebinyk, S.; Grahovac, M.; Mojićević, M.; Grahovac, J. Pepper bacterial spot control by *Bacillus velezensis*: Bioprocess solution. *Microorganisms* **2020**, *8*, 1463. [CrossRef]
12. Grahovac, J.; Pajčin, I.; Vlajkov, V.; Rončević, Z.; Dodić, J.; Cvetković, D.; Jokić, A. *Xanthomonas campestris* biocontrol agent: Selection, medium formulation and bioprocess kinetic analysis. *Chem. Ind. Chem. Eng. Q.* **2021**, in press. [CrossRef]

13. Prabakaran, G.; Hoti, S.L. Application of different downstream processing methods and their comparison for the large-scale preparation of *Bacillus thuringiensis* var. *israelensis* after fermentation for mosquito control. *Biologicals* **2008**, *36*, 412–415. [CrossRef]
14. Brar, S.K.; Verma, M.; Tyagi, R.D.; Valéro, J.R. Recent advances in downstream processing and formulations of *Bacillus thuringiensis* based biopesticides. *Process Biochem.* **2006**, *41*, 323–342. [CrossRef]
15. Qi, L.; Hu, Y.; Chai, Q.; Wang, Q. Enhanced filtration performance and anti-biofouling properties of antibacterial polyethersulfone membrane for fermentation broth concentration. *J. Ind. Eng. Chem.* **2019**, *72*, 346–353. [CrossRef]
16. Shimizu, Y.; Matsushita, K.; Watanabe, A. Influence of shear breakage of microbial cells on cross-flow microfiltration flux. *J. Ferment. Bioeng.* **1994**, *78*, 170–174. [CrossRef]
17. Jana, A.; Ghosh, S.; Majumdar, S. Energy efficient harvesting of *Arthrospira* sp. using ceramic membranes: Analyzing the effect of membrane pore size and incorporation of flocculant as fouling control strategy. *J. Chem. Technol. Biotechnol.* **2018**, *93*, 1085–1096. [CrossRef]
18. Aspelund, M.T.; Rozeboom, G.; Heng, M.; Glatz, C.E. Improving permeate flux and product transmission in the microfiltration of a bacterial cell suspension by flocculation with cationic polyelectrolytes. *J. Membr. Sci.* **2008**, *324*, 198–208. [CrossRef]
19. Salama, A. Modeling of flux decline behavior during the filtration of oily-water systems using porous membranes: Effect of pinning of nonpermeating oil droplets. *Sep. Purif. Technol.* **2018**, *207*, 240–254. [CrossRef]
20. Fan, R.; Ebrahimi, M.; Quitmann, H.; Czermak, P. Lactic acid production in a membrane bioreactor system with thermophilic *Bacillus coagulans*: Fouling analysis of the used ceramic membranes. *Sep. Sci. Technol.* **2015**, *50*, 2177–2189. [CrossRef]
21. Zhang, Y.; Fu, Q. Algal fouling of microfiltration and ultrafiltration membranes and control strategies: A review. *Sep. Purif. Technol.* **2018**, *203*, 193–208. [CrossRef]
22. Chang, Y.-R.; Lee, D.J. Coagulation–membrane filtration of *Chlorella vulgaris* at different growth phases. *Dry. Technol.* **2012**, *30*, 1317–1322. [CrossRef]
23. Marzban, R.; Saberi, F.; Shirazi, M.M.A. Microfiltration and ultrafiltration of *Bacillus thuringiensis* fermentation broth: Membrane performance and spore crystal recovery approaches. *Braz. J. Chem. Eng.* **2016**, *33*, 783–791. [CrossRef]
24. Jokić, A.; Zavargo, Z.; Šereš, Z.; Tekić, M. The effect of turbulence promoter on cross-flow microfiltration of yeast suspensions: A response surface methodology approach. *J. Membr. Sci.* **2010**, *350*, 269–278. [CrossRef]
25. Jokić, A.; Pajčin, I.; Grahovac, J.; Lukić, N.; Dodić, J.; Rončević, Z.; Šereš, Z. Improving energy efficiency of *Bacillus velezensis* broth microfiltration in tubular ceramic membrane by air sparging and turbulence promoter. *J. Chem. Technol. Biotechnol.* **2020**, *95*, 1110–1115. [CrossRef]
26. Jokić, A.; Pajčin, I.; Grahovac, J.; Lukić, N.; Ikonić, B.; Nikolić, N.; Vljakov, V. Dynamic modeling using artificial neural network of *Bacillus Velezensis* broth cross-flow microfiltration enhanced by air-sparging and turbulence promoter. *Membranes* **2020**, *10*, 372. [CrossRef]
27. Tanaka, T.; Usui, K.; Kouda, K.; Nakanishi, K. Filtration behaviors of rod-shaped bacterial broths in unsteady-state phase of cross-flow filtration. *J. Chem. Eng. Jpn.* **1996**, *29*, 973–981. [CrossRef]
28. Guerra, A.; Jonsson, G.; Rasmussen, A.; Waagner Nielsen, E.; Edelman, D. Low cross-flow velocity microfiltration of skim milk for removal of bacterial spores. *Int. Dairy J.* **1997**, *7*, 849–861. [CrossRef]
29. Tomasula, P.M.; Mukhopadhyay, S.; Datta, N.; Porto-Fett, A.; Call, J.E.; Luchansky, J.B.; Renye, J.; Tunick, M. Pilot-scale crossflow-microfiltration and pasteurization to remove spores of *Bacillus anthracis* (Sterne) from milk. *J. Dairy Sci.* **2011**, *94*, 4277–4291. [CrossRef]
30. Kim, S.-H.; Min, C.-S. Fouling reduction using the resonance vibration in membrane separation of whole milk. *J. Ind. Eng. Chem.* **2019**, *75*, 123–129. [CrossRef]
31. Jiang, B.; Hu, B.; Yang, N.; Zhang, L.; Sun, Y.; Xiao, X. Study of turbulence promoters in prolonging membrane life. *Membranes* **2021**, *11*, 268. [CrossRef]
32. Cabassud, C.; Laborie, S.; Durand-Bourlier, L.; Lainé, J.M. Air sparging in ultrafiltration hollow fibers: Relationship between flux enhancement, cake characteristics and hydrodynamic parameters. *J. Membr. Sci.* **2001**, *181*, 57–69. [CrossRef]
33. Hwang, K.-J.; Wu, Y.J. Flux enhancement and cake formation in air-sparged cross-flow microfiltration. *Chem. Eng. J.* **2008**, *139*, 296–303. [CrossRef]
34. Hwang, K.-J.; Hsu, C.-E. Effect of gas–liquid flow pattern on air-sparged cross-flow microfiltration of yeast suspension. *Chem. Eng. J.* **2009**, *151*, 160–167. [CrossRef]
35. Cui, Z.F.; Wright, K.I.T. Flux enhancements with gas sparging in downwards crossflow ultrafiltration: Performances and mechanisms. *J. Membr. Sci.* **1996**, *117*, 109–116. [CrossRef]
36. Mercier, M.; Fonade, C.; Lafforquet-Delorme, C. How slug flow can enhance the ultrafiltration flux in mineral tubular membranes. *J. Membr. Sci.* **1997**, *128*, 103–113. [CrossRef]
37. Mercier-Bonin, M.; Lagane, C.; Fonade, C. Influence of a gas/liquid two-phase flow on the ultrafiltration and microfiltration performances: Case of a ceramic flat sheet membrane. *J. Membr. Sci.* **2000**, *180*, 93–102. [CrossRef]
38. Gupta, B.S.; Hasan, S.; Hashim, M.A.; Cui, Z.F. Effects of colloidal fouling and gas sparging on microfiltration of yeast suspension. *Bioprocess. Biosyst. Eng.* **2005**, *27*, 407–413. [CrossRef]
39. Sur, H.W.; Cui, Z.F. Enhancement of microfiltration of yeast suspensions using gas sparging—Effect of feed conditions. *Sep. Purif. Technol.* **2005**, *41*, 313–319. [CrossRef]

40. Hwang, K.-J.; Chen, L. Effect of air-sparging on the cross-flow microfiltration of microbe/protein bio-suspension. *J. Taiwan Inst. Chem. Eng.* **2010**, *41*, 564–569. [CrossRef]
41. Mikulášek, P.; Pospíšil, P.; Dolecek, P.; Cakl, J. Gas–liquid two-phase flow in microfiltration mineral tubular membranes: Relationship between flux enhancement and hydrodynamic parameters. *Desalination* **2002**, *146*, 103–109. [CrossRef]
42. Mercier-Bonin, M.; Gésan-Guizieu, G.; Fonade, C. Application of gas/liquid two-phase flows during cross flow microfiltration of skimmed milk under constant transmembrane pressure conditions. *J. Membr. Sci.* **2003**, *218*, 93–105. [CrossRef]
43. Fouladitajar, A.; Ashtiani, F.Z.; Rezaei, H.; Haghmoradi, A.; Kargari, A. Gas sparging to enhance permeate flux and reduce fouling resistances in cross flow microfiltration. *J. Ind. Eng. Chem.* **2014**, *20*, 624–632. [CrossRef]
44. Javadi, N.; Ashtiani, F.Z.; Fouladitajar, A.; Zenooz, A.M. Experimental studies and statistical analysis of membrane fouling behavior and performance in microfiltration of microalgae by a gas sparging assisted process. *Bioresour. Technol.* **2014**, *162*, 350–357. [CrossRef] [PubMed]
45. Hyder, M.N.; Huang, R.Y.M.; Chen, P. Pervaporation dehydration of alcohol–water mixtures: Optimization for permeate flux and selectivity by central composite rotatable design. *J. Membr. Sci.* **2009**, *326*, 343–353. [CrossRef]
46. Han, H.; Yu, R.; Li, B.; Zhang, Y.; Wang, W.; Chen, X. Multi-objective optimization of corrugated tube with loose-fit twisted tape using RSM and NSGA-II. *Int. J. Heat Mass Transf.* **2019**, *131*, 781–794. [CrossRef]
47. Mercier, M.; Fonade, C.; Lafforgue-Delorme, C. Influence of the flow regime on the efficiency of a gas-liquid two-phase medium filtration. *Biotechnol. Tech.* **1995**, *9*, 853–858. [CrossRef]
48. Tanaka, T.; Abe, K.-I.; Asakawa, H.; Yoshida, H.; Nakanishi, K. Filtration characteristics and structure of cake in crossflow filtration of bacterial suspension. *J. Ferment. Bioeng.* **1994**, *78*, 455–461. [CrossRef]
49. Huisman, I.H.; Trägårdh, C. Particle transport in crossflow microfiltration—I. Effects of hydrodynamics and diffusion. *Chem. Eng. Sci.* **1999**, *54*, 271–280. [CrossRef]
50. Mota, M.; Teixeira, J.A.; Yelshin, A. Influence of cell-shape on the cake resistance in dead-end and cross-flow filtrations. *Sep. Purif. Technol.* **2002**, *27*, 137–144. [CrossRef]
51. Hwang, K.-J.; Yu, Y.-H.; Lu, W.-M. Cross-flow microfiltration of submicron microbial suspension. *J. Membr. Sci.* **2001**, *194*, 229–243. [CrossRef]
52. Tanaka, T.; Abe, K.-I.; Nakanishi, K. Shear-induced arrangement of cells in cake during crossflow filtration of *Escherichia coli* cells. *Biotechnol. Tech.* **1994**, *8*, 57–60. [CrossRef]
53. Goel, T.; Vaidyanathan, R.; Haftka, R.T.; Shyy, W.; Queipo, N.V.; Tucker, K. Response surface approximation of Pareto optimal front in multi-objective optimization. *Comput. Methods Appl. Mech. Eng.* **2007**, *196*, 879–893. [CrossRef]



Article

Kenics Static Mixer Combined with Gas Sparging for the Improvement of Cross-Flow Microfiltration: Modeling and Optimization

Aleksandar Jokić, Nataša Lukić *, Ivana Pajčin, Vanja Vlajkov, Selena Dmitrović and Jovana Grahovac

Faculty of Technology Novi Sad, University of Novi Sad, Bulevar cara Lazara 1, 21000 Novi Sad, Serbia; jokic@uns.ac.rs (A.J.); ivana.pajcin@uns.ac.rs (I.P.); vanja.vlajkov@uns.ac.rs (V.V.); selena.dmitrovic@uns.ac.rs (S.D.); johana@uns.ac.rs (J.G.)

* Correspondence: nlukic@tf.uns.ac.rs

Abstract: The use of membrane filtration as a downstream process for microbial biomass harvesting is hampered due to the low permeate flux values achieved during the microfiltration of fermentation broths. Several hydrodynamic methods for increasing permeate flux by creating turbulent flow patterns inside the membrane module are used to overcome this problem. The main goal of this study was to investigate the combined use of a Kenics static mixer and gas sparging during cross-flow microfiltration of *Bacillus velezensis* IP22 cultivation broth. Optimization of the microfiltration process was performed by using the response surface methodology. It was found that the combined use of a static mixer and gas sparging leads to a considerable increase in the permeate flux, up to the optimum steady-state permeate flux value of $183.42 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ and specific energy consumption of $0.844 \text{ kW} \cdot \text{h} \cdot \text{m}^{-3}$. The optimum steady-state permeate flux is almost four times higher, whilst, at the same time, the specific energy consumption is almost three times lower compared to the optimum results achieved using gas sparging alone. The combination of Kenics static mixer and gas sparging during cross-flow microfiltration is a promising technique for the enhancement of steady-state permeate flux with simultaneously decreasing specific energy consumption.

Keywords: microfiltration; static mixer; gas sparging; response surface methodology; desirability function; permeate flux; specific energy consumption; microbial biopesticide; *Bacillus velezensis*

1. Introduction

Biopesticides production depends on the method of cultivation broth downstream processing for sustainable and cost-effective use in agriculture [1]. Cultivation broth clarification in order to harvest microbial cells is the first step in downstream processing with the aim of concentrating the active component in the final biopesticide product. In biopesticides biotechnological production, this step is usually carried out by centrifugation or microfiltration [2].

One of the major drawbacks of microfiltration membrane processes that limit its extensive usage is mass transfer resistance through the membrane due to concentration polarization and membrane fouling. The most noticeable outcome of concentration polarization and membrane fouling is the decrease in permeate flux during cross-flow microfiltration due to the adsorption onto the membrane surface and inside the membrane pores. An essential step in restoring membrane permeability is membrane cleaning [3]. However, the capital and operating costs associated with frequent cleaning procedures, as well as the aggressiveness of cleaning, which causes damage to membrane surface, have steered researchers into developing techniques for permeate flux augment. Hence, a large number of research papers focus on the development of hydrodynamic methods for permeate flux enhancement by generating a turbulent flow pattern inside the membrane module, making it less susceptible to fouling [4–9].

Among hydrodynamic methods, turbulence promoters are by far the most commonly used method to increase permeate flux during cross-flow microfiltration. Turbulence

promoters used to increase permeate flux can move within the membrane (dynamic) or be fixed relative to the membrane surface (static). Of the two types of turbulence promoters, static turbulence promoters are more investigated than dynamic turbulence promoters due to their numerous advantages: simpler installation, longer lifespan, lower investment and operational costs, and a wider range of operating feed flow rates and viscosities [10,11]. Static mixers increase permeate flux by splitting and redistributing the fluid flow inside the membrane, and, hence, by improving mixing in the radial and tangential direction, increasing the shear rate and inducing secondary flows near the membrane surface [12].

Besides static mixers, gas sparging is another technique that is employed as a means to successfully hinder membrane fouling and improve permeate flux [4,7–9,13–21]. By injecting gas into the feed, a two-phase (gas–liquid) flow inside the membrane module is created. As a result of forming bubbles inside the membrane module, local eddies are induced and shear rate at the membrane surface is increased [9]. The amount of induced shear rate mostly depends on gas and liquid phase linear speed, as well as bubble diameter and gas–liquid flow regime [22]. The presence of gas bubbles in the membrane channel causes efficient removal of loosely bound macromolecules and particles, while breaking of the cake layer could be caused by gas bubbles bursting or coalescence [6,7].

Combining the two methods for improving permeate flux can result in even greater enlargement by amplifying the fouling mitigation capabilities of both methods [9]. There have been very few studies on the combination of static mixer and gas sparging during membrane filtration [9,23,24]. Derradji et al. [23] investigated the ultrafiltration of a polymer solution (sodium alginate) combining two-phase gas–liquid flow with a Sulzer turbulence promoter placed before the membrane. The results indicated that the combination of Sulzer static mixer and gas sparging ensures a well-mixed two-phase flow which results in high permeate flux. Oil/water emulsion was another feed used in ultrafiltration with combined usage of static mixer and gas sparging [24]. Although in the case of oil/water emulsion, gas sparging does not seem to be very effective for flux enhancement, it was found that combining gas sparging and the use of the static mixer (Kenics) resulted in high permeate fluxes with low energy consumption.

Armbruster et al. [9] investigated the effect of gas sparging, Kenics mixers, a combination of gas sparging with Kenics mixers and a novel concept, the aerating Kenics mixer (combining mixer and sparging in one single device). The combination of a Kenics mixer with gas sparging yielded the highest reduction in fouling for filtration of an aqueous solution of 30 mg·L^{−1} humic acid sodium salt. The authors concluded that the range of economical operation is considerably widened, whilst high flux operation is enabled by the application of static mixers and external air-sparging, or with aerating static mixers.

Response Surface Methodology (RSM) is an efficient method to determine the connection between factors affecting a process and the output response variables of that process [25]. It provides a way of selecting a few points in the design space to efficiently represent the experimental space and, in that way, reduces the number of experimental runs for investigating the factor influences and interactions between them on the selected response. RSM was successfully applied in several subject areas connected to membrane processes, such as membrane synthesis optimization [26,27], optimization of chemical cleaning [28] and membrane performance [29–32].

The main objective of this study was to combine Kenics static mixer and gas sparging (SMGS) to improve permeate flux during cross-flow microfiltration of *Bacillus velezensis* IP22 cultivation broth. For assessing the optimal potential for flux improvement, response surface methodology was applied, i.e., desirability function approach. It was expected that optimum operational parameters could expand the main limitations of gas sparging, providing a viable answer for a high flux and low-energy broth microfiltration method.

2. Materials and Methods

2.1. Production of *Bacillus velezensis* Cultivation Broth

Bacillus velezensis IP22, the strain used as an active component of microbial biopesticide, was isolated from fresh cheese and previously identified using 16S rRNA gene

sequencing [33]. A detailed description of the cultivation of *Bacillus velezensis* IP22 in the bioreactor is given in our previous work [4].

Microfiltration separation efficiency and *Bacillus velezensis* cells viability were evaluated by the standard plate count method and by measuring the absorbance (optical density) of the cultivation broth, retentate and permeate at a wavelength of 600 nm. The concentration of *Bacillus velezensis* (g/L) was calculated using biomass dry weight and the volume of cultivation broth, retentate or permeate sample (20 mL), which was centrifuged [4].

2.2. Microfiltration Experimental Setup

The experimental setup for *Bacillus velezensis* IP22 cultivation broth cross-flow microfiltration was described in detail in our previous publication [34]. All microfiltration experiments were performed at 25 °C and with recirculation of retentate and permeate to maintain a constant volume of the feed mixture. The ceramic membrane (Tami Deutschland, Hermsdorf, Germany) used in the experiments had the following characteristics: length 250 mm, inner diameter 6 mm, outer diameter 10 mm, pore size 200 nm and specific surface area 0.00433 m². The Kenics static mixer used in the experiments had 30 mixing elements with a diameter of 5 mm and a total length of 230 mm. It consists of a series of helical mixing elements made from thin, flat strips, twisted through 180° to form helices. Helices turned around their main axis by 90° against the next element [35]. The pressurized air was introduced into the feed flow channel through the three-way valve without the diffuser. The air flow rate was measured by the mass flow controller type EL-FLOW F-201AV, with an accuracy of ±0.5% (Bronkhorst, The Netherlands). During cross-flow microfiltration, the time (t) necessary for gathering 20 mL permeate (V) through the specific membrane surface area (A) was measured and the flux value (J, L·m⁻²·h⁻¹) was calculated [4]:

$$J = \frac{V}{A \cdot t} \quad (1)$$

Specific energy consumption (E, kW·h·m⁻³) is equal to the ratio of sum of hydraulic and pneumatic powers to the permeate flow rate and it was calculated according to Equation (2) [4]:

$$E = \frac{Q_L \cdot (P_S - P_D) + \frac{\gamma}{\gamma-1} \cdot P_D \cdot Q_{G,D} \cdot \left[\left(\frac{P_S}{P_D} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right]}{J \cdot A} \quad (2)$$

where Q_L (m³·h⁻¹) is the feed flow rate, P_S (Pa) is pressure at the beginning of the membrane module, P_D (Pa) is pressure at the end of the membrane module, $Q_{G,D}$ (m³·h⁻¹) is the air flow rate at the pressure at the end of the membrane module (P_D), γ is the specific heat ratio for air (1.4), J (m³·m⁻²·h⁻¹) is permeate flux and A (m²) is the specific membrane area.

2.3. Experimental Data Analysis—Modeling and Optimization

The effects of transmembrane pressure (TMP: 0.2–1 bar), superficial feed velocity (V_L : 0.53–1.59 m·s⁻¹) and superficial air velocity (V_G : 0.0–0.46 m·s⁻¹) were investigated by applying Box–Behnken's experimental plan (Table 1). Selected responses were steady-state permeate flux and specific energy consumption. Experimental results were fitted using the second-degree polynomial models. Model adequacy was analyzed using the factorial ANOVA (analysis of variance). Coefficients and models were assessed by p -values, while the quality of the experimental data fitting was estimated using the Lack-of-fit, Pure error and R^2 (coefficient of determination) values. All statistical analyses were performed at the significance level of 95% using the Statistica software (v. 13.5, Dell, Round Rock, TX, USA). The polynomial RSM models are usually used for optimization by the desirability function approach [26,27,35]. The Design-Expert software, v. 8.1 (Stat-Ease, Inc., Minneapolis,

MN, USA) was used for generating the polynomial RSM models and optimization by the desirability function approach.

Table 1. Box–Behnken’s experimental plan for broth SMGS microfiltration experiments.

Experiment	Factors—Independent Variables			Responses—Dependent Variables	
	TMP (bar)	V _L (m·s ^{−1})	V _G (m·s ^{−1})	J (L·m ^{−2} ·h ^{−1})	E (kW·h·m ^{−3})
1	0.2	0.53	0.23	48.5	1.6
2	1.0	0.53	0.23	68.0	1.5
3	0.2	1.59	0.23	96.3	3.9
4	1.0	1.59	0.23	156	3.2
5	0.2	1.06	0.0	56.0	1.9
6	1.0	1.06	0.0	110	3.9
7	0.2	1.06	0.46	78.7	3.4
8	1.0	1.06	0.46	120	1.3
9	0.6	0.53	0.0	64.9	1.1
10	0.6	1.59	0.0	127	2.6
11	0.6	0.53	0.46	84.6	0.8
12	0.6	1.59	0.46	140	2.6
13	0.6	1.06	0.23	55.0	4.3
14	0.6	1.06	0.23	52.0	4.5
15	0.6	1.06	0.23	56.0	4.2

TMP—transmembrane pressure, V_L—superficial feed velocity, V_G—superficial gas velocity, J—steady-state permeate flux, E—specific energy consumption

3. Results

The Box–Behnken design with three factors at three levels and three replications in the central point (Table 1) was used as the experimental design to evaluate the effect of microfiltration operational conditions (transmembrane pressure, TMP – X₁, superficial feed velocity, V_L – X₂, and superficial air velocity, V_G – X₃) on steady-state permeate flux (J) and specific energy consumption (E). It included 15 experiments, and the experimental results were fitted with the second order polynomial model shown by Equation (3):

$$Y = b_0 + \sum_{i=1}^3 b_i X_i + \sum_{i=1}^3 b_{ii} X_i^2 + \sum_{i=1}^2 \sum_{j=1}^3 b_{ij} X_i X_j \quad (3)$$

where b_0 is the intercept term, b_i are linear, b_{ii} are quadratic and b_{ij} are interaction effects, X_i are input variables while Y is the response variable for either permeate flux or specific energy consumption.

The results of fitting, including estimated values of linear (b_1, b_2, b_3), quadratic (b_{11}, b_{22}, b_{33}) and interaction (b_{12}, b_{13}, b_{23}) model coefficients with their p -values, are listed in Table 2. The entries in bold font represent statistically significant coefficients at a level of 95% (p -values < 0.05). It is evident from the presented results that the linear effects of all input variables, the interaction effects of transmembrane pressure and superficial feed velocity, as well as the quadratic effects of all three input variables have statistically significant effects on steady-state permeate flux. In the case of a model for specific energy consumption, linear effect of superficial feed velocity, interaction between transmembrane pressure and superficial feed velocity, and all three quadratic effects are statistically significant.

The obtained models were tested by performing the analysis of variance (ANOVA). According to ANOVA (Table 3), the proposed regression models for permeate flux and specific energy consumption during microfiltration of *Bacillus velezensis* IP22 cultivation broth with the combination of Kenics static mixer and gas sparging are statistically significant, with p -values less than 0.05. Furthermore, high determination coefficients ($R^2 > 0.98$) for both models indicate their excellent ability to predict response variable behavior.

Table 2. Coefficients of regression models for steady-state permeate flux and specific energy consumption for broth SMGS microfiltration experiments.

Effects	Steady-State Permeate Flux ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$)			Specific Energy Consumption ($\text{kW}\cdot\text{h}\cdot\text{m}^{-3}$)		
	Coefficient Actual	Coded	<i>p</i> -Value	Coefficient Actual	Coded	<i>p</i> -Value
Intercept b_0	126.2	54.33	0.0002	−6.49	4.313	0.0002
Linear						
b_1	−81.22	21.81	<0.0001	6.46	−0.112	0.220
b_2	−157.3	31.66	<0.0001	11.87	0.912	<0.0001
b_3	−141.2	8.18	0.0024	15.98	−0.175	0.081
Quadratic						
b_{11}	77.86	12.46	0.0020	−2.85	−0.457	0.012
b_{22}	90.45	25.41	<0.0001	−4.65	−1.307	0.0001
b_{33}	460.9	24.38	<0.0001	−23.28	−1.232	0.0001
Interaction						
b_{12}	47.41	10.05	0.0043	−0.708	−0.15	0.244
b_{13}	−34.51	−3.18	0.1797	−11.14	−1.025	0.0003
b_{23}	−13.74	−1.68	0.4482	0.615	0.075	0.538

Table 3. ANOVA of regression models for steady-state permeate flux and specific energy consumption for broth SMGS microfiltration experiments.

Source	Response	DF	SS	MS	F-Value	<i>p</i> -Value
Model	J ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$)	9	17364.6	1929.4	116.33	<0.0001
	E ($\text{kW}\cdot\text{h}\cdot\text{m}^{-3}$)	9	22.662	2.518	48.805	0.0002
Residual	J ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$)	5	82.93	16.58		
	E ($\text{kW}\cdot\text{h}\cdot\text{m}^{-3}$)	5	0.258	0.052		
Lack-of-fit	J ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$)	3	74.26	24.75	5.712	0.153
	E ($\text{kW}\cdot\text{h}\cdot\text{m}^{-3}$)	3	0.202	0.068	2.434	0.304
Pure error	J ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$)	2	8.667	4.333		
	E ($\text{kW}\cdot\text{h}\cdot\text{m}^{-3}$)	2	0.055	0.028		
Total	J ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$)	14	17447.5			
	E ($\text{kW}\cdot\text{h}\cdot\text{m}^{-3}$)	14	22.920			
		R²	Adj. R²	Pred. R²	Adeq. Precision	
		J ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$)	0.995	0.987	0.931	32.163
		E ($\text{kW}\cdot\text{h}\cdot\text{m}^{-3}$)	0.989	0.969	0.853	19.955

J—steady-state permeate flux, E—specific energy consumption, DF—degree of freedom, SS—sum of squares, MS—mean squares, R²—coefficient of determination

The ANOVA results given in Table 3 show that the coefficient of determination was 0.995 and 0.989 for second-degree polynomial models for permeate flux and specific energy consumption, respectively. The model for permeate flux could explain 99.5% of the variation in response, whilst for specific energy consumption, the value is 98.9%, which indicates the excellent fitness of the models. The predicted R² of 0.931 is in reasonable agreement with the adjusted R² of 0.987 for permeate flux, whilst in the case of specific energy consumption, the predicted R² of 0.853 is also in good agreement with the adjusted R² of 0.969. Adequate precision compares the range of the predicted values at the design points to the average prediction error; a ratio greater than 4 indicates adequate model discrimination. In this study, ratios of 32.163 and 19.955 for steady-state permeate flux and specific energy consumption, respectively, indicate an adequate signal.

Based on the ANOVA of the regression, both models are significant. In the case of steady-state permeate flux, a high F-value (116.33) and a low *p*-value (*p* < 0.0001) were observed, as well as a non-significant lack-of-fit (*p*-value of 0.153). For specific energy consumption, an F-value of 48.81 and *p*-value of 0.0002 imply that the model is significant,

along with a non-significant lack-of-fit (p -value of 0.304). Furthermore, small values of pure error (8.667 for permeate flux and 0.055 for specific energy consumption) indicated that variation caused by measurement error is insignificant.

Therefore, the selected regression models could be used to analyze trends of responses. Second-degree polynomial models could be successfully applied to describe the effects of transmembrane pressure, superficial feed velocity and superficial air velocity on steady-state permeate flux and specific energy consumption during SMGS cross-flow microfiltration.

Independent variables interactive effects on the steady-state permeate flux and specific energy consumption are illustrated by the 3D response surface plots (Figures 1 and 2).

The parity plot for steady-state permeate flux is shown in Figure 1a. As it can be seen, the second-degree polynomial model shows good agreement between experimental and predicted flux values. Figure 1b,c show the effects of transmembrane pressure (X1) with feed (X2) and gas (X3) velocities on the permeate flux, respectively. It can be seen (Figure 1b), that the maximum values of permeate flux are obtained for the highest transmembrane pressure and superficial feed velocity values. The steady-state flux increases with the increase in both feed velocity as well as TMP, indicating a strong synergistic effect between these variables (Figure 1b). On the other side, the increase in gas velocity resulted in lower flux improvements compared to the feed superficial velocity rise (Figure 1c). Transmembrane pressure in both cases had a positive effect on the flux enhancement. The influence of superficial feed and gas velocities on steady-state permeate flux is depicted in Figure 1d. The increase in both superficial velocities shows the positive effects on steady-state permeates flux.

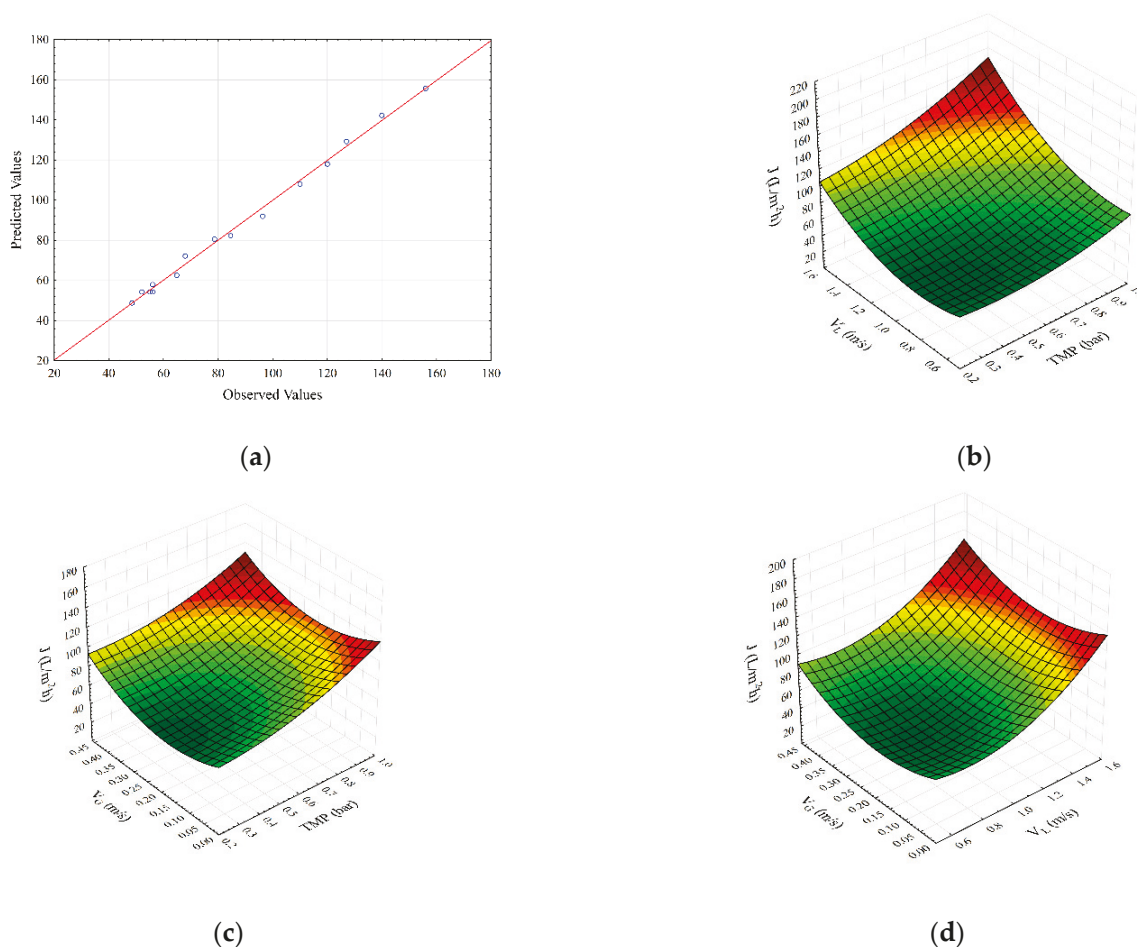


Figure 1. Parity plot (a) and response surface plots (b–d) representing the regression model for steady-state permeate flux during SMGS microfiltration of *Bacillus velezensis* IP22 cultivation broth.

The parity plot for specific energy consumption is shown in Figure 2a. As can be seen, the second-degree polynomial model shows good agreement between experimental and predicted flux values. Figure 2b,c show the effects of transmembrane pressure with feed and gas velocities on the specific energy consumption, respectively. It can be seen (Figure 2b) that maximum values of specific energy consumption are obtained for the highest superficial feed velocity values and lower transmembrane pressure values. The specific energy consumption increases with the increase in transmembrane pressure at lower superficial air velocities. On the other hand, at higher TMP values, specific energy consumption decreases at higher air velocities (Figure 2c). The influence of superficial feed and gas velocities on specific energy consumption is represented in Figure 2d. An increase in both superficial velocities results in a decline in specific energy consumption.

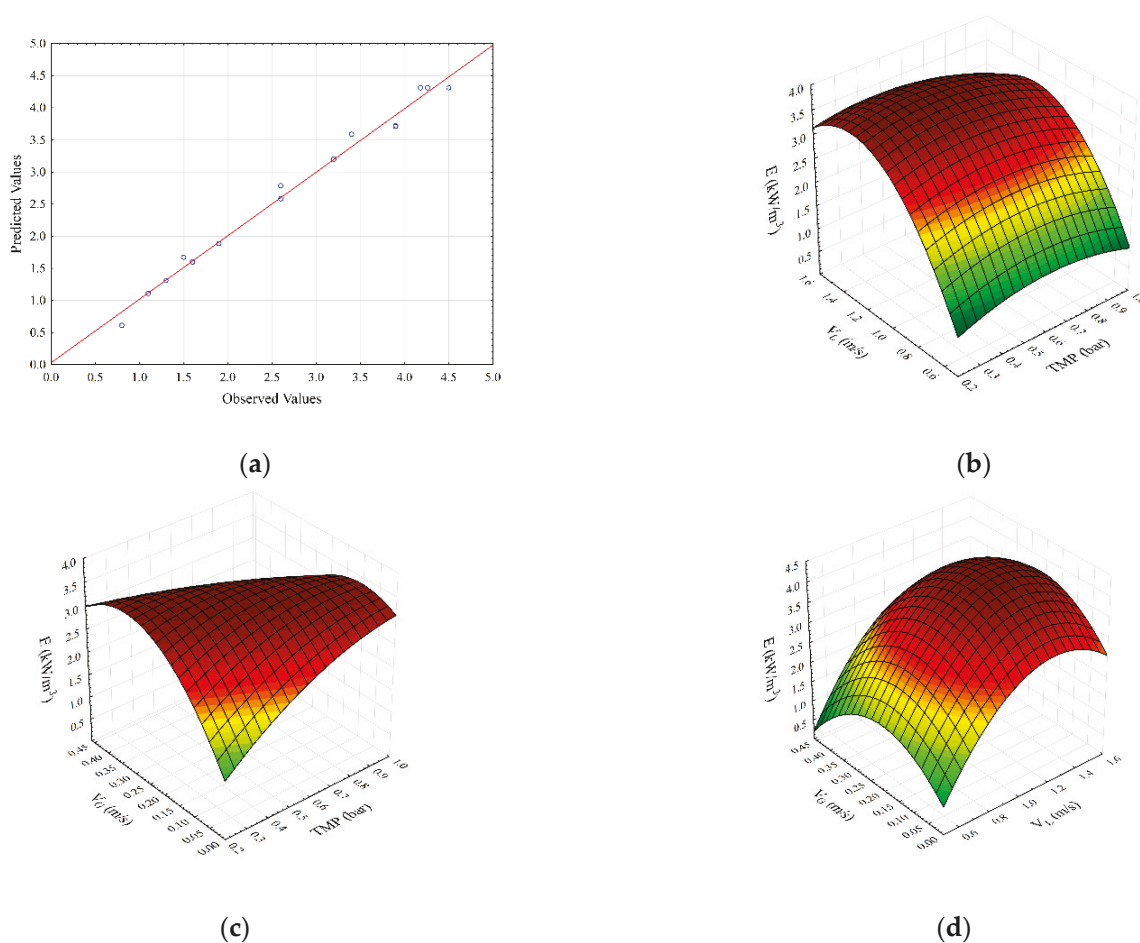


Figure 2. Parity plot (a) and response surface plots (b–d) representing the regression model for specific energy consumption during SMGS microfiltration of *Bacillus velezensis* IP22 cultivation broth.

In this study, a desirability function method was applied for simultaneous optimization of investigated responses during SMGS microfiltration of *Bacillus velezensis* IP22 cultivation broth. Here, the maximum for steady-state permeate flux and the minimum for specific energy consumption were combined into one measurement called the desirability function. The selected responses were transformed to individual desirability values in a range from 0 to 1. The overall desirability of the process was computed as a geometric mean of the individual desirability functions [35]. The optimization results of the desirability function method are listed in Table 4. It can be seen that the maximum permeate flux and minimum specific energy consumption can be attained at the highest investigated factor levels: transmembrane pressure of 1 bar, superficial feed velocity of 1.59 m·s^{−1} and superficial gas velocity of 0.46 m·s^{−1}. The high value of the overall desirability function (0.99) indi-

cates that both optimization goals (maximum permeate flux and minimum specific energy consumption) were successfully accomplished. The predicted values of optimum permeate flux and specific energy consumption were $183.42 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and $0.844 \text{ kW}\cdot\text{h}\cdot\text{m}^{-3}$, respectively. On the other hand, in our previous study of microfiltration, assisted only by gas sparging [4], the optimum values for steady-state permeate flux of $48.57 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and specific energy consumption of $2.37 \text{ kW}\cdot\text{h}\cdot\text{m}^{-3}$ were predicted. By comparing the optimization results of SMGS microfiltration with the microfiltration, assisted only by gas sparging, it can be concluded that the presence of a static mixer considerably amounts to higher steady-state permeate flux and lower specific energy consumption.

Table 4. Optimization results obtained by the desirability function approach during SMGS microfiltration of *Bacillus velezensis* IP22 cultivation broth.

Factors—Independent Variables	Goal	Optimized Value
Transmembrane pressure, TMP (bar)	in range	1.0
Superficial feed velocity, V_L ($\text{m}\cdot\text{s}^{-1}$)	in range	1.59
Superficial air velocity, V_G ($\text{m}\cdot\text{s}^{-1}$)	in range	0.46
Responses—Dependent Variables	Goal	Predicted Value
Steady-state permeate flux, J ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$)	maximize	183.42
Specific energy consumption, E ($\text{kW}\cdot\text{h}\cdot\text{m}^{-3}$)	minimize	0.844
Desirability function		0.99

Cell viability and concentration analyses have shown that *Bacillus velezensis* cells have been completely retained by the microfiltration membrane. Concentration of *Bacillus velezensis* biomass in the fresh cultivation broth was $0.37 \text{ g}\cdot\text{L}^{-1}$, while after the filtration experiments, biomass concentration in the retentate was $0.36 \text{ g}\cdot\text{L}^{-1}$. Spectrophotometric measurements (OD_{600}) also confirmed this fact, and the absorbance values were 0.82 for the fresh cultivation broth and 0.78 for the retentate sample after microfiltration experiments. According to the results of the standard plate count method, *Bacillus velezensis* cells did not suffer either a significant change in the cell concentration or a decrease in cell viability due to increased shear stress caused by the mixer and air-sparging effects.

4. Discussion

Based on Figure 1b–d, the influence of operating conditions on steady-state permeate flux can be seen. With increasing transmembrane pressure, steady-state permeate flux increases for all values of superficial feed velocity (Figure 1b). With an increase in transmembrane pressure at lower values of superficial feed velocity, an increase in permeate flux is around 47%, whilst at higher values of superficial feed velocity, an increase in flux value is about 70%. The increases in steady-state permeate flux values were detected in the whole transmembrane pressure experimental range, contrary to the results obtained in the case of gas sparging without a static mixer [4]. In the case of gas sparging alone, the increase in transmembrane pressure lowers the steady-state flux due to the cell arrangement for smaller superficial feed velocity [4]. As reported in the literature, rod-shaped particles, such as *Bacillus velezensis*, tend to be oriented parallel to flow in the membrane channel so that they exhibit higher specific resistance and, consequently, lower flux values, even for the increased TMP [5,36–38]. When combining gas sparging with the static mixer, turbulence in the membrane channel is present, even for low feed velocities, so, in this way, orientation of rod-shaped particles, i.e., shear induced arrangement, is hindered from the start of the microfiltration process. In this way, flux is enhanced by reducing filtration cake resistance to permeate flow.

The effects of transmembrane pressure and superficial air velocity on the steady-state permeate flux are given in Figure 1c. At lower transmembrane pressure values, the increase in permeate flux is about 60%, while at higher values, the transmembrane pressure increase in permeate flux is only about 10%. The reason for this behavior can

be found in the resistance of the filtration cake to the flow of smaller cultivation broth components. The combination of a Kenics mixer with gas sparging generated an increase in flux values in the whole range of superficial air values. Once again, the presence of a Kenics mixer had a decisive influence on flow conditions inside the membrane channel. The two-phase flow generated as a result of introducing air bubbles into the feed results in flux enhancement [4,6–8,39]. As reported in the literature, secondary induced flow patterns play a major role in the enhancement. It promotes local mixing influencing the flow in the membrane channel and thus reducing the resistance to mass transfer across the membrane [40]. In the case of gas sparging alone, a flux increase was observed up to a value of $0.25 \text{ m}\cdot\text{s}^{-1}$ for superficial air velocity [4], while in the case of experiments with the mixer and gas sparging combination, the flux increase was observed even for the velocities increased beyond this threshold. The cake structure becomes more compact (the particle packing becomes more regular) under the gas sparging [4,41], resulting in lower permeate flux, while the cake arrangement is avoided by the turbulence generated in the presence of a static mixer. At the highest superficial gas velocity, an enhancement in steady-state permeate flux of about 40% is observed, so more prominent improvement was achieved in comparison to only a 14% increase in a system with gas sparging alone [4].

The influence of superficial feed velocity and superficial gas velocity on steady-state permeate flux is depicted in Figure 1d. The insertion of the turbulence promoter into the membrane channel affects the flow of air bubbles within it, so the change in flow pattern causes significant differences in system performance. The steady-state flux values are significantly higher compared to gas sparging alone. The change in flow pattern through the membrane channel by inserting the Kenics static mixer results in smaller bubbles passing through the membrane channel closer to the membrane surface. Otherwise, smaller air bubbles would tend to stay grouped in the middle section of the membrane channel away from the membrane surface [42]. So, in this way, bubbles additionally contribute to the removal of the surface filtration cake along with the static mixer [9]. By increasing the values of superficial gas velocity up to $0.25 \text{ m}\cdot\text{s}^{-1}$, a plateau in permeate flux was reached in the case of gas sparging alone [4]. In the case of combining the effects of a static mixer and gas sparging, the plateau region was not observed. As the superficial air velocity rises, so larger bubbles are formed, creating slugs in the membrane channel. In the slug region of flow conditions, further increases in bubbles size, only increase the length of the slug which has no effect on wake size and does not contribute to the increased membrane surface scouring [42]. As a result, increasing superficial air velocity above $0.25 \text{ m}\cdot\text{s}^{-1}$ has little effect on permeate flux. Oppositely, when the static mixer is placed in the membrane channel, the flux rise is observed at all feed superficial velocities with increasing superficial air velocities (Figure 1d), suggesting that the Kenics mixer ensures a better mixing of the two-phase flow. Namely, the presence of a static mixer prevents the formation of larger air plugs. However, a higher increase in steady-state permeate flux (about 25%) was observed at lower superficial feed velocities, compared to the increase in steady-state permeate flux at higher values of superficial feed velocities (about 7%).

The influence of transmembrane pressure and superficial feed velocity on specific energy consumption is shown in Figure 2b. At lower superficial feed velocities, the effect of transmembrane pressure is insignificant. On the other hand, at the highest superficial feed velocity, by increasing the transmembrane pressure, a decrease in specific energy consumption occurs, due to the synergistic effect of both variables on the increase of permeate flux. As expected, an increase in superficial feed velocity leads to the sharp enhancement of specific energy consumption (up to 140%) for the whole range of investigated transmembrane pressure.

The influence of transmembrane pressure and superficial gas velocity on specific energy consumption is illustrated in Figure 2c. At lower superficial gas velocities, the values of specific energy consumption increased by about 100% by increasing the value of transmembrane pressure. Opposite to that, at higher superficial gas velocities, a further increase in transmembrane pressure decreases specific energy consumption. The lowest

value of specific energy consumption of about $1.3 \text{ kW}\cdot\text{h}\cdot\text{m}^{-3}$ is obtained at the highest transmembrane pressure and highest values of superficial gas velocity. The possible explanation for this behavior is in fact that the two-phase gas–liquid flow has greater influence on membrane surface cleaning. Compared to the microfiltration assisted only by gas sparging [4], in which the reduction in specific energy consumption under the operating conditions (high transmembrane pressure and superficial gas velocity) amounted to 52%, in microfiltration experiments with a combination of static mixer and gas sparging, a decrease in specific energy consumption is more significant and amounts to about 100%.

The simultaneous influence of superficial feed and gas velocity on specific energy consumption is shown in Figure 2d. At lower superficial gas velocities, specific energy consumption increases. Given that a bubbly flow regime exists under these conditions, streamlined movement of bubbles due to the specific construction of Kenics static mixer does not contribute significantly to changes in the structure of the filtration cake layer, so the flux is not high enough to reduce energy consumption per m^3 . Therefore, specific energy consumption increases when lower permeate flux is achieved. However, in the slug gas–liquid flow regime, a different behavior is observed. Due to the effect of Kenics static mixer on slug flow, a significant increase in flux occurs, resulting in a decrease in specific energy consumption.

Optimization of operational conditions for SMGS microfiltration suggested that the optimum conditions are at the upper side of the experimental range of all variables. Contrary to the results of our previous study on microfiltration assisted only by gas sparging, significantly higher permeate flux values are accomplished with simultaneously lowering the specific energy consumption in the case of SMGS microfiltration. The optimum values of steady permeate flux are almost four times higher than in the case of applying gas sparging alone. On the other hand, high flux values result in a significant decrease in a specific energy consumption (per m^3); in SMGS case almost three times lower, compared to the optimum specific energy consumption in gas sparging alone [4]. An additional experiment was conducted to validate the optimal solution for maximum permeate flux. The results of the verification experiment are in good agreement with the desirability function approach. The experimental values of optimum permeate flux and specific energy consumption were $178.53 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and $0.882 \text{ kW}\cdot\text{h}\cdot\text{m}^{-3}$, respectively.

5. Conclusions

The present study reports on the influence of combining Kenics static mixer and gas sparging on the performance of *Bacillus velezensis* IP22 cultivation broth cross-flow microfiltration. The study results confirm the achievement of the main goal, given that the combined use of a static mixer and gas sparging leads to a considerable increase in the permeate flux. Two-phase gas–liquid flow was completely altered in the presence of Kenics static mixer, resulting in a significant steady-state permeate flux improvement.

The optimization results for the maximum permeate flux and minimum specific energy consumption were attained at the highest investigated factor levels: transmembrane pressure of 1 bar, superficial feed velocity of $1.59 \text{ m}\cdot\text{s}^{-1}$ and superficial gas velocity of $0.46 \text{ m}\cdot\text{s}^{-1}$. The overall desirability function of 0.99 indicates that both optimization goals were accomplished. The predicted values of optimum steady-state permeate flux and specific energy consumption were $183.42 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and $0.844 \text{ kW}\cdot\text{h}\cdot\text{m}^{-3}$, respectively. The optimum steady-state permeate flux is almost four times higher, whilst at the same time, specific energy consumption is almost three times lower compared to the optimum results achieved using gas sparging alone.

Author Contributions: Conceptualization, A.J. and I.P.; methodology, J.G. and I.P.; software, N.L.; validation, A.J., I.P. and J.G.; formal analysis, S.D. and V.V.; investigation, I.P., V.V. and S.D.; resources, A.J., J.G. and N.L.; data curation, A.J. and N.L.; writing—original draft preparation, A.J. and N.L.; writing—review and editing, A.J., N.L. and J.G.; visualization, N.L.; supervision, I.P.; project administration, J.G.; funding acquisition, A.J., N.L., S.D. and J.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia, grant number 451-03-68/2022-14/200134.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

- Prabakaran, G.; Hoti, S.L. Application of different downstream processing methods and their comparison for the large-scale preparation of *Bacillus thuringiensis* var. *israelensis* after fermentation for mosquito control. *Biologicals* **2008**, *36*, 412–415. [CrossRef] [PubMed]
- Brar, S.K.; Verma, M.; Tyagi, R.D.; Valéro, J.R. Recent advances in downstream processing and formulations of *Bacillus thuringiensis* based biopesticides. *Process Biochem.* **2006**, *41*, 323–342. [CrossRef]
- Bartlett, M.; Bird, M.R.; Howell, J.A. An experimental study for the development of a qualitative membrane cleaning model. *J. Membr. Sci.* **1995**, *105*, 147–157. [CrossRef]
- Jokić, A.; Pajčin, I.; Lukić, N.; Vlajkov, V.; Kiralj, A.; Dmitrović, S.; Grahovac, J. Modeling and Optimization of Gas Sparging-Assisted Bacterial Cultivation Broth Microfiltration by Response Surface Methodology and Genetic Algorithm. *Membranes* **2021**, *11*, 681. [CrossRef] [PubMed]
- Jokić, A.; Pajčin, I.; Grahovac, J.; Lukić, N.; Dodić, J.; Rončević, Z.; Šereš, Z. Energy efficient turbulence promoter flux-enhanced microfiltration for the harvesting of rod-shaped bacteria using tubular ceramic membrane. *Chem. Eng. Res. Des.* **2019**, *150*, 359–368. [CrossRef]
- Hwang, K.-J.; Wu, Y.-J. Flux enhancement and cake formation in air-sparged cross-flow microfiltration. *Chem. Eng. J.* **2008**, *139*, 296–303. [CrossRef]
- Hwang, K.-J.; Hsu, C.-E. Effect of gas–liquid flow pattern on air-sparged cross-flow microfiltration of yeast suspension. *Chem. Eng. J.* **2009**, *151*, 160–167. [CrossRef]
- Mercier, M.; Fonade, C.; Lafforgue-Delorme, C. How slug flow can enhance the ultrafiltration flux in mineral tubular membranes. *J. Membr. Sci.* **1997**, *128*, 103–113. [CrossRef]
- Armbruster, S.; Brochard, A.; Lölsberg, J.; Yüce, S.; Wessling, M. Aerating static mixers prevent fouling. *J. Membr. Sci.* **2019**, *570–571*, 537–546. [CrossRef]
- Krstić, D.; Tekić, M.; Carić, M.; Milanović, S. Kenics Static Mixer as Turbulence Promoter in Cross-Flow Microfiltration of Skim Milk. *Sep. Sci. Technol.* **2003**, *38*, 1549–1560. [CrossRef]
- Krstić, D.; Tekić, M.N.; Carić, M.D.; Milanović, S.D. Static turbulence promoter in cross-flow microfiltration of skim milk. *Desalination* **2004**, *163*, 297–309. [CrossRef]
- Armbruster, S.; Stockmeier, F.; Junker, M.; Schiller-Becerra, M.; Yüce, S.; Wessling, M. Short and spaced twisted tapes to mitigate fouling in tubular membranes. *J. Membr. Sci.* **2020**, *595*, 117426. [CrossRef]
- Cui, Z.F.; Wright, K.I.T. Flux enhancements with gas sparging in downwards crossflow ultrafiltration: Performance and mechanism. *J. Membr. Sci.* **1996**, *117*, 109–116. [CrossRef]
- Cabassud, C.; Laborie, S.; Lainé, J.M. How slug flow can improve ultrafiltration flux in organic hollow fibres. *J. Membr. Sci.* **1997**, *128*, 93–101. [CrossRef]
- Bellara, S.R.; Cui, Z.F.; Pepper, D.S. Gas sparging to enhance permeate flux in ultrafiltration using hollow fibre membranes. *J. Membr. Sci.* **1996**, *121*, 175–184. [CrossRef]
- Gupta, B.S.; Hasan, S.; Hashim, M.A.; Cui, Z.F. Effects of colloidal fouling and gas sparging on microfiltration of yeast suspension. *Bioprocess. Biosyst. Eng.* **2005**, *27*, 407–413. [CrossRef]
- Sur, H.W.; Cui, Z.F. Enhancement of microfiltration of yeast suspensions using gas sparging—effect of feed conditions. *Sep. Purif. Technol.* **2005**, *41*, 313–319. [CrossRef]
- Mikulášek, P.; Pospíšil, P.; Doleček, P.; Cakl, J. Gas–liquid two-phase flow in microfiltration mineral tubular membranes: Relationship between flux enhancement and hydrodynamic parameters. *Desalination* **2002**, *146*, 103–109. [CrossRef]
- Fouladitajar, A.; Zokaee Ashtiani, F.; Rezaei, H.; Haghmoradi, A.; Kargari, A. Gas sparging to enhance permeate flux and reduce fouling resistances in cross flow microfiltration. *J. Ind. Eng. Chem.* **2014**, *20*, 624–632. [CrossRef]
- Javadi, N.; Zokaee Ashtiani, F.; Fouladitajar, A.; Moosavi Zenooz, A. Experimental studies and statistical analysis of membrane fouling behavior and performance in microfiltration of microalgae by a gas sparging assisted process. *Bioresour. Technol.* **2014**, *162*, 350–357. [CrossRef]
- Alsahy, Q.F.; Albyati, T.M.; Zablouk, M.A. A Study of the Effect of Operating Conditions on Reverse Osmosis Membrane Performance with and without Air Sparging Technique. *Chem. Eng. Commun.* **2013**, *200*, 1–19. [CrossRef]

22. Cabassud, C.; Laborie, S.; Durand-Bourlier, L.; Lainé, J.M. Air sparging in ultrafiltration hollow fibers: Relationship between flux enhancement, cake characteristics and hydrodynamic parameters. *J. Membr. Sci.* **2001**, *181*, 57–69. [CrossRef]
23. Derradji, A.F.; Bernabeu-Madico, A.; Taha, S.; Dorange, G. The effect of a static mixer on the ultrafiltration of a two-phase flow. *Desalination* **2000**, *128*, 223–230. [CrossRef]
24. Vatai, G.N.; Krstic, D.M.; Höflinger, W.; Koris, A.K.; Tekic, M.N. Combining air sparging and the use of a static mixer in cross-flow ultrafiltration of oil/water emulsion. *Desalination* **2007**, *204*, 255–264. [CrossRef]
25. Lazic, Z.R. *Design of Experiments in Chemical Engineering: A Practical Guide*; Wiley: Hoboken, NJ, USA, 2006.
26. Mohammed Redha, Z.; Bu-Ali, Q.; Saeed, Y.A.; Ali, A.M. Optimization of the Asymmetric Cellulose Acetate Membrane Synthesis Variables for Porosity and Pure Water Permeation Flux Using Response Surface Methodology: Microfiltration Application. *Arab. J. Sci. Eng.* **2021**, *46*, 6593–6607. [CrossRef]
27. Wang, X.; Wang, Q.; Zhao, M.; Zhang, L.; Ji, X.; Sun, H.; Sun, Y.; Ma, Z.; Xue, J.; Gao, X. Fabrication of a Cation-Exchange Membrane via the Blending of SPES/N-Phthaloyl Chitosan/MIL-101(Fe) Using Response Surface Methodology for Desalination. *Membranes* **2022**, *12*, 144. [CrossRef]
28. Jung, J.; Ko, Y.-H.; Choi, J.-S.; Lee, S. Optimization of chemical cleaning condition for microfiltration process using response surface methodology. *Desalination Water Treat.* **2016**, *57*, 7466–7478. [CrossRef]
29. Waqas, S.; Harun, N.Y.; Bilad, M.R.; Samsuri, T.; Nordin, N.A.H.M.; Shamsuddin, N.; Nandiyanto, A.B.D.; Huda, N.; Roslan, J. Response Surface Methodology for Optimization of Rotating Biological Contactor Combined with External Membrane Filtration for Wastewater Treatment. *Membranes* **2022**, *12*, 271. [CrossRef]
30. Live Lozada, G.S.; García López, A.I.; Martínez-Férez, A.; Ochando-Pulido, J.M. On the modeling and optimization of two-phase olive-oil washing wastewater treatment and polyphenols recovery by ceramic tubular microfiltration membranes. *J. Environ. Manag.* **2022**, *316*, 115227. [CrossRef]
31. Belgada, A.; Charik, F.Z.; Achiou, B.; Ntambwe Kambuyi, T.; Alami Younssi, S.; Beniazza, R.; Dani, A.; Benhida, R.; Ouammou, M. Optimization of phosphate/kaolinite microfiltration membrane using Box–Behnken design for treatment of industrial wastewater. *J. Environ. Chem. Eng.* **2021**, *9*, 104972. [CrossRef]
32. Rajewski, J.; Dobrzyńska-Inger, A. Application of Response Surface Methodology (RSM) for the Optimization of Chromium(III) Synergistic Extraction by Supported Liquid Membrane. *Membranes* **2021**, *11*, 854. [CrossRef] [PubMed]
33. Pajčin, I.; Vlajkov, V.; Frohme, M.; Grebinyk, S.; Grahovac, M.; Mojićević, M.; Grahovac, J. Pepper Bacterial Spot Control by *Bacillus velezensis*: Bioprocess Solution. *Microorganisms* **2020**, *8*, 1463. [CrossRef] [PubMed]
34. Jokić, A.; Pajčin, I.; Grahovac, J.; Lukić, N.; Dodić, J.; Rončević, Z.; Šereš, Z. Improving energy efficiency of *Bacillus velezensis* broth microfiltration in tubular ceramic membrane by air sparging and turbulence promoter. *J. Chem. Technol. Biotechnol.* **2020**, *95*, 1110–1115. [CrossRef]
35. Jokić, A.; Zavargo, Z.; Šereš, Z.; Tekić, M. The effect of turbulence promoter on cross-flow microfiltration of yeast suspensions: A response surface methodology approach. *J. Membr. Sci.* **2010**, *350*, 269–278. [CrossRef]
36. Fan, R.; Ebrahimi, M.; Quitmann, H.; Czermak, P. Lactic Acid Production in a Membrane Bioreactor System with Thermophilic *Bacillus coagulans*: Fouling Analysis of the Used Ceramic Membranes. *Sep. Sci. Technol.* **2015**, *50*, 2177–2189. [CrossRef]
37. Mota, M.; Teixeira, J.A.; Yelshin, A. Influence of cell-shape on the cake resistance in dead-end and cross-flow filtrations. *Sep. Purif. Technol.* **2002**, *27*, 137–144. [CrossRef]
38. Li, C.; Guo, Y.; Shen, L.; Ji, C.; Bao, N. Scalable concentration process of graphene oxide dispersions via cross-flow membrane filtration. *Chem. Eng. Sci.* **2019**, *200*, 127–137. [CrossRef]
39. Mercier-Bonin, M.; Lagane, C.; Fonade, C. Influence of a gas/liquid two-phase flow on the ultrafiltration and microfiltration performances: Case of a ceramic flat sheet membrane. *J. Membr. Sci.* **2000**, *180*, 93–102. [CrossRef]
40. Cui, Z.F.; Wright, K.I.T. Gas–liquid two-phase cross-flow ultrafiltration of BSA and dextran solutions. *J. Membr. Sci.* **1994**, *90*, 183–189. [CrossRef]
41. Hwang, K.-J.; Chen, L. Effect of air-sparging on the cross-flow microfiltration of microbe/protein bio-suspension. *J. Taiwan Inst. Chem. Eng.* **2010**, *41*, 564–569. [CrossRef]
42. Li, Q.Y.; Cui, Z.F.; Pepper, D.S. Effect of bubble size and frequency on the permeate flux of gas sparged ultrafiltration with tubular membranes. *Chem. Eng. J.* **1997**, *67*, 71–75. [CrossRef]



Article

Modeling and Structural Optimization of MSF-RO Desalination System

Lu He ¹, Aipeng Jiang ^{1,*}, Qiuyun Huang ¹, Yan Zhao ², Chuang Li ¹, Jian Wang ¹ and Yudong Xia ¹

¹ School of Automation, Hangzhou Dianzi University, Hangzhou 310018, China; 202060285@hdu.edu.cn (L.H.); hqy09092020@163.com (Q.H.); lichuang_1006@163.com (C.L.); 02016@hdu.edu.cn (J.W.); 42072@hdu.edu.cn (Y.X.)

² Chn Energy Lucency Enviro-Tech Co., Ltd., Beijing 100039, China; 12030975@chnenergy.com.cn

* Correspondence: jiangaipeng@hdu.edu.cn; Tel.: +86-0571-8691-9133

Abstract: Based on the mathematical modeling and operational optimization studies of reverse osmosis (RO) and multistage flash (MSF) desalination, the structural optimization of the hybrid process was specially studied in this work with the consideration of reducing comprehensive expenses under given operational conditions. Firstly, according to the process mechanism and flowchart of the RO and MSF seawater desalination technologies, seven hybrid structures with different feed conditions were designed, and their connection equations were established for numerical calculation. Then, in order to evaluate the economic performance of the hybrid systems with different structures, the hourly average operational cost equations of RO and MSF processes were established and formulated as the comprehensive evaluation indicators. Next, with a given water production requirement, simulation calculations of the hybrid system with seven different structures were performed. The results show that the hybrid system with the fourth structure has the lowest operational cost of 4.6834 CNY/m³, and at the same time it has the lowest blowdown. However, if we take GOR or production water temperature as the target, the optimal structure of the hybrid system is the fifth or the seventh option. The obtained results are helpful in structural optimization of the hybrid system with aspects of operational cost reduction, maximum GOR, or minimizing the wastewater discharge.

Keywords: desalination; MSF; RO; operational cost; modeling; simulation; structural optimization

1. Introduction

The lack of fresh water resources is an indisputable fact, and desalination technology is an effective strategy to solve this problem [1,2]. At present, among many seawater desalination technologies, multistage flash (MSF), and reverse osmosis seawater (SWRO) desalination are the most effectively and widely technologies used in practice. However, with the increased requirement of cost-saving and wastewater discharge reduction, new challenges are presented to improve seawater desalination process [3]. Since the MSF technique [4,5] can get a large amount of higher quality fresh water from low-grade energy and its concentration is significantly lower than that of the SWRO technique, the good complementary characteristics of these two techniques become an attractive direction to improve the overall profits for freshwater achievement with lower operational costs. At present, the MSF technology and SWRO technology are relatively mature, and there are some studies about the hybrid thermal-membrane desalination technology, but the detailed research on the optimal structure of the hybrid system is relatively novel and deficient [6]. Since both the SWRO desalination and the MSF desalination are energy-intensive technologies, most new studies are focused on the couple of desalination technique with the energy-driven system. For example, Khan et al. [7,8] carried out fruitful work on the desalination system coupled with nuclear power. In their studies, a techno-economic analysis of

a nuclear power plant coupled with RO or MED or RO + MED and even RO + MSF systems were assessed in detail. With the consideration of environmental impact, they also built a simulation model for calculation and assessment of the socio-economic and environmental impacts of a nuclear desalination system.

In many regions where there are no renewable energies or nuclear energy available, the hybrid desalination technologies for full utilization of energy and cost saving were also studied by researchers. Kuenstle et al. [9] proposed a design concept for a combined MSF-RO and power plant system. They evaluated its economic benefits, and concluded that the combined system has lower water production costs than a single MSF system. Al-marafie [10] carried out the economic comparison between MSF and MSF-RO seawater desalination systems—the results showed that the MSF-RO system has more advantageous than MSF. In addition, the author proposed that replacement of the local traditional desalination system with the MSF-RO system has better application prospects. Awerbuch et al. [11] studied the SWRO desalination system and MSF-RO hybrid seawater desalination system, and designed two MSF-RO and one MSF-RO-VEC seawater desalination systems with different coupling structures. In the same year, Awerbuch et al. [12] designed a hybrid system, analyzed the characteristics of the MSF desalination system and RO desalination system, and after 1987, the authors still affirmed the advantages of the MSF-RO seawater desalination system and gave a structure diagram of the initially designed hybrid system. In the same year, Al-Mutaz et al. [13] designed a relatively simple MSF-RO system and established the system model. However, it has not been verified and simulated, and the subsequent system optimization work has not been carried out. El-Sayed et al. [14] designed the MSF-RO experimental device and analyzed and studied the experimental data. After 1800 h of experimental testing, the experimental data proved the superiority of the MSF-RO system in terms of desalination rate, fresh water output, and energy conservation. However, this conclusion can only be regarded as a qualitative background, not enough to draw a specific conclusion, and further research is needed. However, at least based on our literature knowledge, the above work did not carry detailed model-based numerical analysis on the optimal design and operation of systems. A reasonable and accurate mathematical model, which can fully describe the important process parameters and their influences, is very important for the study of the subsequent system. Most of the above research work affirms the superiority of the MSF-RO system, but at least based on our literature knowledge, the above work does not carry out detailed model-based numerical analysis for optimal system design and operation.

For the detailed quantitative analysis and performance prediction requirement to guide the hybrid system's application, a series of modeling, simulation, and optimization works have been carried out at home and abroad. The relevant characteristics of the hot-film hybrid system is deeply understood by using the calculation tool. Cardona et al. [15] studied the changes in energy saving and water production cost after the integration of the MSF system and RO system. Based on the established water production model, the levels of energy consumption and water production before and after the system integration were obtained, which emphasized the advantages of MSF-RO in energy saving. Helal et al. [16–18] established seven different coupling forms of the MSF-RO seawater desalination system, in addition to a two-stage SWRO seawater desalination system model and a BR-MSF seawater desalination model. Finally, various schemes are compared and evaluated, and it is concluded that through integrating MSF with the SWRO technique, the water production cost of the system can be reduced by 17% to 24%. Marcovecchio et al. [19] established a simple hybrid MSF-RO desalination system with reference to the work of Helal and others, taking the highest daily fresh water output as the optimization goal and solving it. The MSF part of the model was the OT-MSF seawater desalination system, which had a simple structure. Only the discharge of the MSF system and the feed of the RO system are coupled, and the coupling mode is relatively single. Vince et al. [20] established a super-model of the MSF-RO seawater desalination system, and proposed a method of optimization problem decomposition and realization of multiobjective optimization. This method combined

process modeling and process integration technology with advanced mathematical solving tools to simultaneously optimize the configuration and operation of the integrated desalination system. Moreover, this method has been verified in the model established in this paper. Abdulrahim et al. [21] used the first and second laws of thermodynamics to conduct a rigorous modeling and simulation study on the hybrid MSF-RO system. The results showed that the performance of the MSF-RO integrated system had been enhanced. The study considered four optimization goals, namely the maximum fresh water production, the minimum water production cost, the maximum gain ratio, and the minimum exergy damage rate; and the genetic algorithm was used to optimize the multiobjectives to make this system meet the requirements.

Wu et al. [22] adopted the concept of hybrid nodes and distribution nodes, and established a superstructure model of the MSF and RO seawater desalination system. Regarding the water production ratio as an optimization variable of the integrated system, an improved genetic algorithm was used to get the optimal solution. Malik et al. [23] used the Aspen custom modeling tool (ACM, V8.4.) to model and simulate MSF, RO, and MSF-RO respectively. The author took the lowest economic objective function as the optimization goal, and optimized the system operating conditions and process design variables. However, in his study, only one simple MSF-RO coupled structure was considered. For application intention, Boushi [24] studied two system transformation schemes for the current status of the MSF plant in Al Taweelah A2 in Abu Dhabi, UAE. Based on practical data and the performance model of MSF, RO, and MSF-RO systems, the techno-economics and environmental impact were analyzed. To realize detailed numerical calculations and global optimization for a more complex system, Bandi et al. [25] used differential evolution algorithm (DE) to globally optimize the MSF-RO desalination system with five different MSF-RO alternative mixing schemes. The results showed that the DE algorithm was suitable for the solving optimization problems of the more complex MSF-RO system. The given system and algorithm can be used to estimate the flowrate, the salt content of blowdown brine, circulating brine flowrate, the salt content, and condensate flowrate.

The above studies have confirmed the advantages and prospects of the MSF-RO system, and carried out relevant work in the aspect of optimal control. However, there are still some works that should be done for better guiding the structural and operational optimization of the MSF-RO system, especially in the plants who need to upgrade their RO or MSF system and achievement better operational profits. In this work, based on our earlier studies of full-scale detailed mechanism models of SWRO and MSF systems, detailed structural optimizations of the MSF-RO system under certain operational conditions and with techno-economics indexes are studied. After establishing the complete mechanism models of MSF and SWRO systems, according to the different feeding, mixture, and separation forms of the MSF-RO system, seven structural combination forms are designed and modeled for numerical calculation, and furthermore, the economic and performance equations are established for comparative analysis and scheme evaluation. Our work is helpful to guide structural optimization and detailed quantitative analysis of the MSF-RO system.

2. Different Structures of Hybrid MSF-RO System and Their Connection Equations

In order to deeply analyze the impact of its feeding mode on the economy of the hybrid MSF-RO seawater desalination system, this paper proposes seven hybrid schemes of the MSF-RO system according to different feeding conditions:

1. The OT-MSF system and SWRO system feed water independently;
2. The BR-MSF system and SWRO system feed water independently;
3. The last stage flash water of the OT-MSF system is the feed water of the SWRO system;
4. The last stage flash water of the BR-MSF system is the feed water of the SWRO system;
5. The brine in the thermal discharge section of the BR-MSF system is used as the feed water of the SWRO system;

6. The rejected water of the SWRO system is used as part of the feed water of the OT-MSF system;
7. The rejected water of the SWRO system is used as part of the feed water of the BR-MSF system.

In order to facilitate the analysis and make the study more targeted, in this work, the MSF desalination adopted 16-stage OT-MSF and BR-MSF systems, respectively. The SWRO system adopted the SW30HR-400i spiral-wound RO modules, and put seven RO modules in each pressure vessel. The whole system depends on the actual situation to determine the number of pressure vessels. Since the mechanism models of MSF process and SWRO process have been established by our earlier work and can be referred in literatures, the model equations of the MSF and SWRO system that were used in our work were not listed in this paper. The steady-state models of OT-MSF and BR-MSF systems can be seen from Mujtaba [26–28], Woldai A [29], Rosso [30], and Gao [31] et al. The steady-state mechanism model of the SWRO system can be seen from Jiang [32–34], Ma [35], and Cheng [36] et al. This paper just shows the different schemes of the hybrid system and the equations to connect the MSF and RO processes, and this is enough to achieve the whole model of the hybrid system under a given coupling structure.

2.1. Hybrid System with Independent Feeding

2.1.1. Scheme of OT-MSF and SWRO System with Independent Feed Water

As is shown in the Figure 1. In the option 1, the hybrid system is composed by OT-MSF and SWRO parts with independent feed water—that is to say, the feed conditions of the two parts are the same, and they are operated almost completely independently of each other.

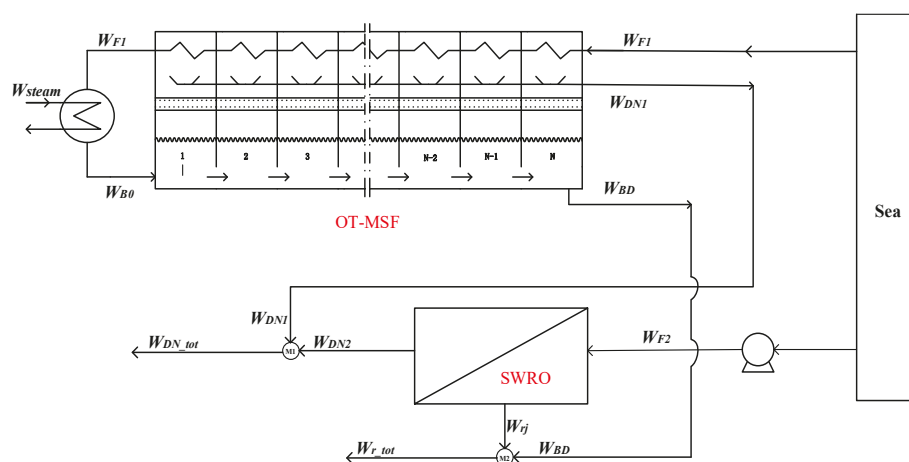


Figure 1. Option 1—the OT-MSF system and SWRO system with independent feed water.

Mixer M₁:

$$W_{DN_tot} = W_{DN1} + W_{DN2} \quad (1)$$

Mixer M₂:

$$W_{r_tot} = W_{rj} + W_{BD} \quad (2)$$

The hybrid option 1 only affects the water production temperature and concentration of the coupling system, and has no effects on the overall water production of the system. It can be used as the basic scheme for hybrid scheme comparison.

2.1.2. The BR-MSF System and SWRO System with Independent Feed Water

As is shown in the Figure 2. The hybrid system is composed by BR-MSF and SWRO parts with independent feed water.

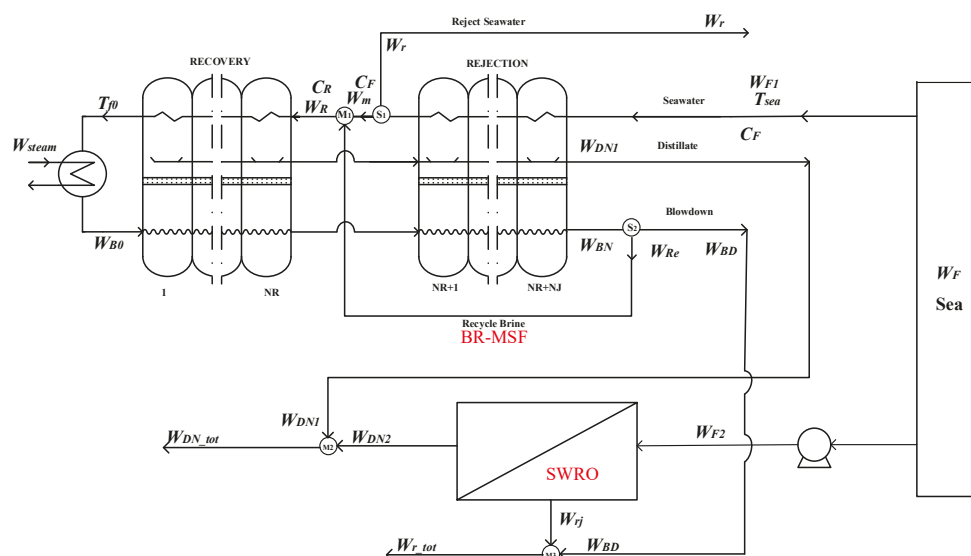


Figure 2. Option 2—the BR-MSF system and SWRO system with independent feed water.

Splitter S_1 :

$$W_m = W_F - W_r \quad (3)$$

Splitter S_2 :

$$W_{BD} = W_{BN} - W_{Re} \quad (4)$$

Mixer M_1 :

$$W_R = W_m + W_{Re} \quad (5)$$

Mixer M₂:

$$W_{DN \text{ tot}} = W_{DN1} + W_{DN2} \quad (6)$$

Mixer M₃:

$$W_{r \text{ tot}} = W_{ri} + W_{BD} \quad (7)$$

In the hybrid option 2, the splitters S_1 , S_2 , and the mixer M_1 are self-owned by the BR-MSF system. As in hybrid option 1, option 2 only couples the system water production and brine water, which has an impact on the water production temperature and concentration of the hybrid system, but has no impact on the overall water production of the system.

2.2. The Last Stage Flash Water of the MSF System as the Feed Water of the SWRO System

2.2.1. The Last Stage Flash Water of the OT-MSF System as the Feed Water of the SWRO System

In the hybrid option 3, part of the blowdown water W_{BD1} in the OT-MSF system is used as the feed water W_{F2} of the SWRO system, removing the seawater pretreatment link in the SWRO system. Its flow chart is shown in Figure 3. The whole coupling system summarizes the water production of the OT-MSF system and the SWRO system. At this time, the overall water production and temperature are affected.

Splitter S_1 :

$$W_{BD1} = W_{BD} - W_{BD2} \quad (8)$$

Mixer M_1 :

$$W_{DN \text{ total}} = W_{DN1} + W_{DN2} \quad (9)$$

Mixer M_2 :

$$W_{r_tot} = W_{ri} + W_{BD2} \quad (10)$$

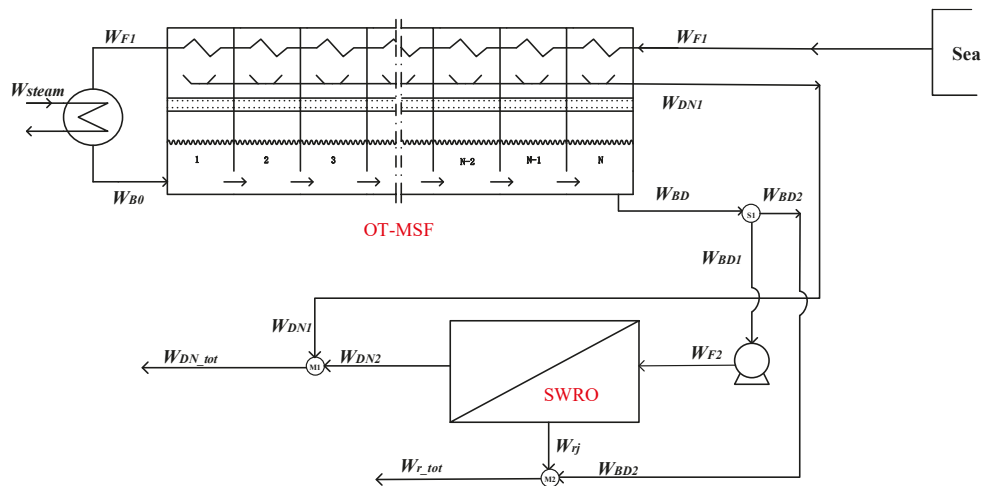


Figure 3. Option 3—the last-stage flash water of the OT-MSF system as the feed water of the SWRO system.

2.2.2. The Last-Stage Flash Water of the BR-MSF System as the Feed Water of the SWRO System

Similarly to the hybrid situation of option 3, in option 4, part of the blowdown water W_{BD1} in the BR-MSF system is used as the feed water W_{F2} of the SWRO system, and the seawater pretreatment in the SWRO system is removed. Its flow chart can be seen in the Figure 4. The whole hybrid system summarizes the water production of the BR-MSF system and the SWRO system. At this time, the overall water production and temperature are affected.

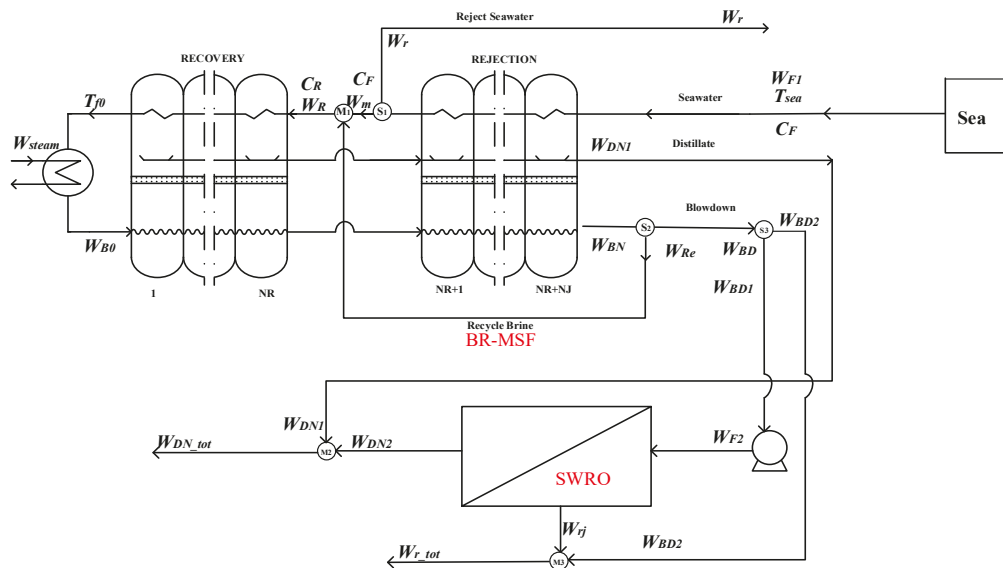


Figure 4. Option 4—the last-stage flash water of the BR-MSF system as the feed water of the SWRO system.

Splitter S_1 :

$$W_m = W_{F1} - W_r \quad (11)$$

Splitter S_2 :

$$W_{BD} = W_{BN} - W_{Re} \quad (12)$$

Splitter S_3 :

$$W_{F2} = W_{BD} - W_{BD2} \quad (13)$$

Mixer M₁:

$$W_R = W_m + W_{Re} \quad (14)$$

Mixer M₂:

$$W_{DN_tot} = W_{DN1} + W_{DN2} \quad (15)$$

Mixer M₃:

$$W_{r_tot} = W_{rj} + W_{BD2} \quad (16)$$

2.3. The Rejected Water of the BR-MSF System as the Feed Water of the SWRO System

The process flow diagram can be seen in the Figure 5. In option 5, part of the rejected water W_{r1} of the BR-MSF system is used as the feed water W_{F2} of the SWRO system. At this time, the temperature of the feed water in the SWRO system is increased, and the whole process of seawater pretreatment is removed. At this time, the entire hybrid system aggregates the production water and wastewater of the two subsystems. At this time, the overall water production and quality of the system are affected.

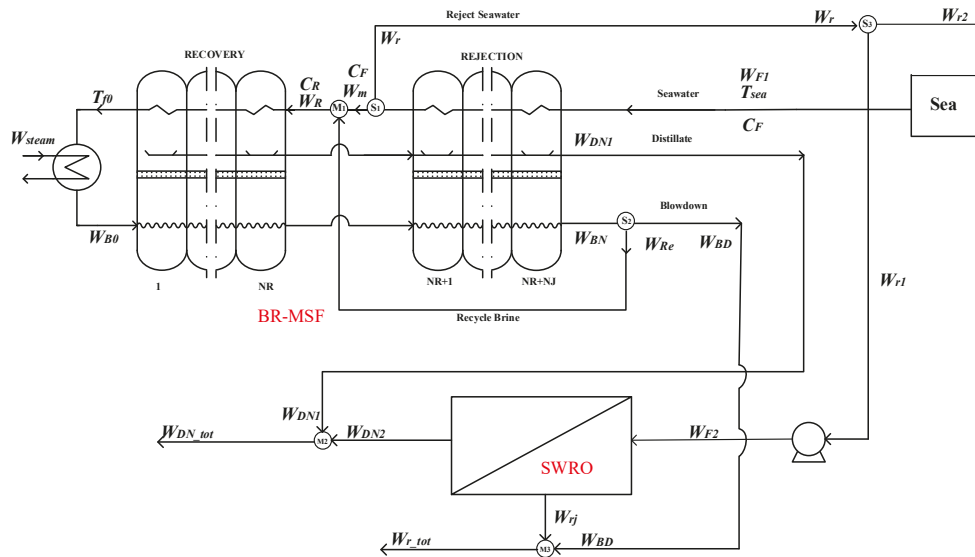


Figure 5. Option 5—the rejected water of BR-MSF system as the feed water of the SWRO system.

Splitter S₁:

$$W_m = W_{F1} - W_r \quad (17)$$

Splitter S₂:

$$W_{BD} = W_{BN} - W_{Re} \quad (18)$$

Splitter S₃:

$$W_{F2} = W_r - W_{r2} \quad (19)$$

Mixer M₁:

$$W_R = W_m + W_{Re} \quad (20)$$

Mixer M₂:

$$W_{DN_tot} = W_{DN1} + W_{DN2} \quad (21)$$

Mixer M₃:

$$W_{r_tot} = W_{rj} + W_{BD2} \quad (22)$$

2.4. The Rejected Water of the SWRO System as Part of the Feed Water of the MSF System

2.4.1. The Rejected Water of the SWRO System as Part of the Feed Water of the OT-MSF System

Among the five options mentioned above, the output of the MSF system is used as the feed water of the SWRO system. Options 6 and 7 are compared, on the other hand, with the wastewater from the SWRO system and part of the seawater as the feed water for the MSF system.

In option 6, the blowdown water W_{rj} of the SWRO system is used as the feed water W_{F1} of the OT-MSF system. Figure 6 shows the flow of this option. In this case, the feeding water conditions of the OT-MSF system are changed, and the overall water production of the hybrid system also changes. The hybrid system combines the water production of the two systems, and the blowdown water of the hybrid system is only discharged from the OT-MSF system.

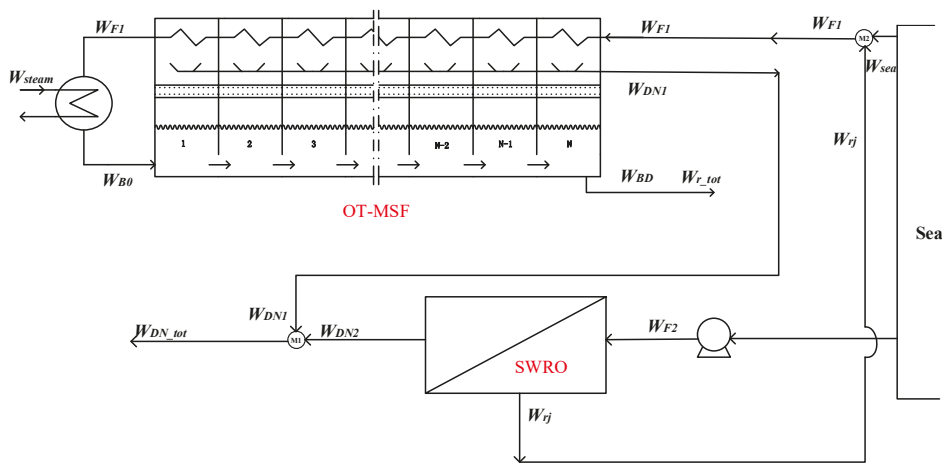


Figure 6. Option 6—the rejected water of the SWRO system as part of the feed water of the OT-MSF system.

Coupling system blowdown:

$$W_{r_tot} = W_{BD} \quad (23)$$

Mixer M₁:

$$W_{DN_tot} = W_{DN1} + W_{DN2} \quad (24)$$

Mixer M₂:

$$W_{F1} = W_{rj} + W_{sea} \quad (25)$$

2.4.2. The Rejected Water of the SWRO System as Part of the Feed Water of the BR-MSF System

In option 7, the blowdown water W_{rj} of the SWRO system is used as the feed water W_{F1} of the BR-MSF system. Figure 7 shows the flow of this option. At this time, the feeding water conditions of the BR-MSF system are changed, and the overall water production of the coupled system also changes. The hybrid system combines the water production of the two systems, and the blowdown water of the hybrid system is only discharged from the BR-MSF system.

Coupling system blowdown:

$$W_{r_tot} = W_{BD} \quad (26)$$

Splitter S₁:

$$W_m = W_{F1} - W_r \quad (27)$$

The cost of chemical agents mainly includes various acid reagents, scale inhibitors, flocculants, and other additives that change the water hardness.

OC_{EN} :

$$OC_{EN} = \left[P_f \cdot W_{F2} / (\eta_{hp} \cdot \eta_{fd}) - P_r \cdot W_{rj} \cdot \eta_{bp} \right] \cdot P_{elc} \quad (34)$$

where P_f denotes the feed water pressure, which is 65 bar; η_{hp} refers to the high-pressure pump efficiency, which is 0.85; η_{fd} is the mechanical efficiency of the variable frequency drive, which is 0.94; P_r is the outlet pressure of concentrated brine; W_{rj} refers to the concentrated brine outlet flowrate; η_{bp} is the booster pump mechanical efficiency, which is 0.8.

OC_{MER} :

$$OC_{MER} = Pri_{ME} \cdot MOD \cdot \zeta_{re} / 365 / 24 \quad (35)$$

where Pri_{ME} is the unit price of the RO membrane, 6200 CNY/group; MOD refers to the total number of RO membranes used in the system; ζ_{re} represents the replacement rate of membrane modules, which is 0.3.

OC_{MN} :

$$OC_{MN} = OC_{MNCON} + OC_{MNCL} \quad (36)$$

$$OC_{MNCL} = N_{cl} \cdot (OC_{OT} + OC_{PC}) / X_{mr} \quad (37)$$

The maintenance cost of the SWRO system is composed of the maintenance cost of conventional equipment OC_{MNCON} and the cleaning and maintenance cost of reverse osmosis membrane module OC_{MNCL} . N_{cl} is the number of membrane module cleanings in a membrane replacement cycle; X_{mr} is the membrane replacement cycle; OC_{OT} is the cost of chemicals in membrane cleaning; OC_{PC} is the system startup and shutdown costs incurred by the cleaning operation.

OC_{LB1} :

$$OC_{LB1} = Pri_{LB} \cdot N_{LB} / 24 \quad (38)$$

$$N_{LB} = W_{DN2} \cdot NP / 100 \quad (39)$$

N_{LB} refers to the number of labors. W_{DN2} represents the water production of the SWRO system, and NP refers to the number of pressure vessels in the system.

OC_{WS2} :

$$OC_{WS2} = 0.025 \cdot W_{rj} \cdot NP \quad (40)$$

where W_{rj} is the blowdown water from the SWRO system.

This article studies the operation plan of the system within the day, and the cost of RO membrane cleaning can be ignored. Therefore, Equation (36) can be rewritten as Equation (41) as shown:

$$OC_{MN} = OC_{MNCON} = 0.03OC_{RO} \quad (41)$$

The total cost of SWRO system can be formulated as follows:

$$\begin{aligned} OC_{RO} &= OC_{IP} + OC_{EN} + OC_{MER} + OC_{MN} + OC_{CH} + OC_{LB1} + OC_{WS1} \\ &= OC_{IP} + OC_{EN} + OC_{MER} + OC_{MNCON} + OC_{CH} + OC_{LB1} + OC_{WS1} \\ &= OC_{IP} + OC_{EN} + OC_{MER} + 0.03OC_{RO} + OC_{CH} + OC_{LB1} + OC_{WS1} \\ &= (OC_{IP} + OC_{EN} + OC_{MER} + OC_{CH} + OC_{LB1} + OC_{WS1}) / 0.97 \end{aligned} \quad (42)$$

3.2. Operational Economic Model of MSF System

Likewise, the economic model of the MSF seawater desalination system is only for the hourly operating cost model. It mainly includes the following six parts, namely:

1. Heating steam, OC_{ST} ;
2. System power consumption cost, OC_{EL} ;
3. Maintenance cost, OC_{MT} ;
4. Pretreatment cost, OC_{PR} ;

5. Maintenance cost, OC_{MN} ;
6. Labor costs, OC_{LB2} ;
7. Wastewater management cost, OC_{WS2} ;

The relevant expression of the corresponding operation cost of each part is as follows:

OC_{ST} :

$$OC_{ST} = 22/24 \cdot W_{steam} \cdot [(T_{steam} - 40)/85] \cdot 0.00415 \cdot 6.4525 \cdot 1.45 \quad (43)$$

The MSF system economic model can be seen from Gao et al. [31], and the corresponding reference is the data in the paper by Wade et al. [37] in 2001. Taking into account the US dollar inflation, the GDP deflator is used for conversion. Areppim website provides a dollar conversion calculator for each year based on the GDP deflator, and the dollar in 2001 is equivalent to \$1.45 in 2021. Based on the exchange rate between USD and RMB at 6.4525, the economic model of MSF seawater desalination system is synthesized, as shown in the following formulas.

OC_{EL} :

$$OC_{EL} = 22/24 \cdot (W_{DN}/\rho_w + 0.005 \cdot W_F/\rho_b) \cdot (P_{elc}/3) \cdot 6.4525 \cdot 1.45 \quad (44)$$

OC_{MT} :

$$OC_{MT} = 22/24 \cdot (W_{DN}/\rho_w) \cdot 0.082 \cdot 6.4525 \cdot 1.45 \quad (45)$$

OC_{PR} :

$$OC_{PR} = 22/24 \cdot (0.15 \cdot W_F/\rho_b + 0.1 \cdot W_{DN}/\rho_w) \cdot 0.024 \cdot 6.4525 \cdot 1.45 \quad (46)$$

OC_{LB2} :

$$OC_{LB2} = 22/24 \cdot (W_{DN}/\rho_w + 0.005 \cdot W_F/\rho_b) \cdot 0.1 \cdot 6.4525 \cdot 1.45 \quad (47)$$

OC_{WS2} :

$$OC_{WS2} = 0.025 \cdot (W_{BD}/\rho_b) \quad (48)$$

The specific cost of the above six parts, which make up the total hourly operational costs of the MSF system can be expressed as:

$$OC_{MSF} = OC_{ST} + OC_{EL} + OC_{MT} + OC_{PR} + OC_{LB2} + OC_{WS2} \quad (49)$$

3.3. Evaluation Indicators and Economic Model Verification

The economic model of MSF-RO system is composed of the economic model of MSF system and SWRO system. In order to evaluate the economy of the hybrid model, the economic models of the OT-MSF system and the SWRO system need to be verified respectively. For the MSF system, the OT-MSF system is selected for economic model verification. This study only discusses the case that the seawater temperature is 25 °C and the electricity price is 0.67 CNY/KW h. The verification premises of the economic model of MSF-RO hybrid system are as follows:

1. The feed seawater flowrate of the OT-MSF system and the SWRO system are both 1.203×10^7 kg/h = 1.203×10^4 m³/h.
2. The heating steam temperature is 97 °C.
3. The feed seawater concentration of the OT-MSF system is 5.7% = 57 kg/m³, and the feed seawater concentration of the SWRO system is 30 kg/m³. Because the pretreatment requirements of the system are inconsistent, the feed seawater concentrations of MSF system and RO system are different.
4. The unit price of single RO membrane of SWRO system is 6200 CNY.

Substitute the above parameters into the SWRO system economic model, and the IPOPT and CONOPT solver of the GAMS platform is called for simulation [38]. The SWRO

system water production and system cost ratio are shown in Tables 1 and 2. And the cost analysis is shown in Figure 8.

Table 1. Water production of the SWRO system.

Parameters	Data
Feed water flowrate (m ³ /h)	12,030
Production flowrate (m ³ /h)	6255.24
Blowdown flowrate (kg/h)	5774.75
Number of pressure vessels	1204
Total number of RO modules	8428
Water production ratio	0.52

Table 2. SWRO system cost ratio table.

Cost	Total Price (CNY)	Unit Price (CNY/m ³)	Proportion
OC_{IP}	1185.31	0.1895	0.0540
OC_{CH}	2827.05	0.4519	0.1289
OC_{EN}	14,284.70	2.2836	0.6513
OC_{MER}	1789.51	0.2861	0.0816
OC_{MN}	657.94	0.1052	0.0300
OC_{LB1}	1042.54	0.1667	0.0475
OC_{WS1}	144.37	0.0231	0.0066
OC_{RO}	21,931.41	3.5061	1

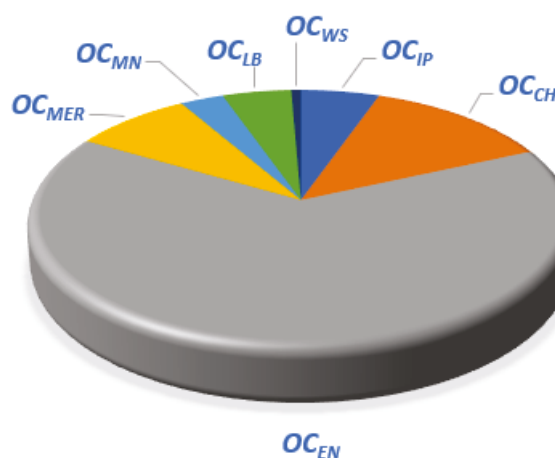


Figure 8. SWRO cost proportion analysis.

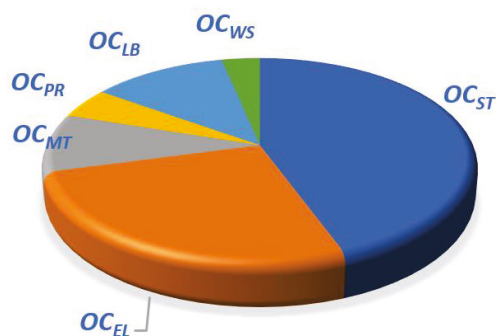
The above parameters were substituted into the OT-MSF system economic model, and simulated on the GAMS platform. The OT-MSF system water production and system cost ratio are shown in Tables 3 and 4. The cost analysis is shown in Figure 9.

Table 3. Water production of the OT-MSF system.

Parameters	Data
Feed water flowrate (m ³ /h)	12,030
Production flowrate (m ³ /h)	1082.24
Heating steam mass flowrate (kg/h)	153,446.00
Blowdown flowrate (kg/h)	10,947.76
Gained output ratio	7.05
Water production ratio	0.09

Table 4. OT-MSF system cost ratio.

Cost	Total Price (CNY)	Unit Price (CNY/m ³)	Proportion
OC_{ST}	3662.41	3.3841	0.4435
OC_{EL}	2188.14	2.0219	0.2649
OC_{MT}	761.11	0.7033	0.0922
OC_{PR}	393.71	0.3638	0.0477
OC_{LB2}	979.76	0.9053	0.1186
OC_{WS2}	273.69	0.2529	0.03314
OC_{MSF}	8258.82	7.6313	1

**Figure 9.** OT-MSF cost proportion analysis.

Under the same water intake flowrate conditions, the total price and cost ratio of the water production cost of SWRO and MSF systems can be obtained, respectively. For the SWRO system, the unit price of water production is 3.51 CNY/m³, and for the OT-MSF system, the unit price of water production is 7.63 CNY/m³. The ratio of the MSF system to the SWRO system's water price is 0.4594, and Fan [39] et al.'s statistical result ratio is 0.4600. Therefore, it is proved that the economic model designed in this study can reflect the economic situation of the system and it can be used for analysis and research. It can be seen from Figure 8 that in the cost of SWRO, the OC_{EN} accounts for the highest proportion of the overall cost, exceeding 50% of the overall cost, and the remaining costs account for a small proportion. It can be seen from Figure 9 that among the OT-MSF costs, the OC_{ST} accounts for the highest proportion of the overall cost, followed by the system power consumption cost, and the remaining costs account for a relatively low proportion. On the whole, the operation cost of SWRO and MSF system is 1:2, and both account for the highest proportion in the power consumption of the two processes.

4. Economic Evaluation of MSF-RO System

In order to quantitatively evaluate the economy and water production performance of the MSF-RO system with different feeding modes, it is necessary to fix the water production and water production ratio of each option. According to the research of Helal et al. [16], assuming that the actual demand ratio of the hybrid seawater desalination plant is 1:2, the MSF system of each hybrid system in this study stipulates that the water production is 1000 m³/h, the SWRO system stipulates that the water production is 2000 m³/h. The relationship between the water production flowrate of the two systems is 1:2, and the overall water production flowrate is 3000 m³/h. The detailed model of the coupled system with different structures are coded and implemented under the platform of GAMS 24.0, and the IPOPT was used as the solver to solve the complex nonlinear programming problems.

4.1. Simulation of the MSF-RO System with Different Structures

4.1.1. The OT-MSF System and SWRO System with Independent Feed Water

The simulation results are shown in Tables 5 and 6. The water production of the hybrid system is shown in Table 7. In this option, the total operating cost of the SWRO system is 7012.21 CNY, of which the running energy consumption accounts for 65.13%. The unit

price of SWRO system water production is 3.5061 CNY/m³. For the OT-MSF system, the total operating cost is 7422.27 CNY, of which the running energy consumption accounts for 27.21%. Additionally, the unit price of OT-MSF water production is 7.4223 CNY/m³. Both systems account for a large proportion of energy consumption costs.

Table 5. SWRO system cost ratio table.

Cost	Total Price (CNY)	Unit Price (CNY/m ³)	Proportion
<i>OC_{IP}</i>	378.98	0.1895	0.0540
<i>OC_{CH}</i>	903.90	0.4519	0.1289
<i>OC_{EN}</i>	4567.25	2.2836	0.6513
<i>OC_{MER}</i>	572.23	0.2861	0.0816
<i>OC_{MN}</i>	210.37	0.1052	0.0300
<i>OC_{LB1}</i>	333.33	0.1667	0.04754
<i>OC_{WS1}</i>	46.16	0.0231	0.0066
<i>OC_{RO}</i>	7012.21	3.5061	1

Table 6. OT-MSF system cost ratio table.

Cost	Total Price (CNY)	Unit Price (CNY/m ³)	Proportion
<i>OC_{ST}</i>	3193.96	3.1940	0.4303
<i>OC_{EL}</i>	2019.28	2.0193	0.2721
<i>OC_{MT}</i>	703.27	0.7033	0.0948
<i>OC_{PR}</i>	355.45	0.3555	0.0479
<i>OC_{LB2}</i>	904.15	0.9042	0.1218
<i>OC_{WS2}</i>	246.15	0.2461	0.0332
<i>OC_{MSF}</i>	7422.27	7.4224	1

Table 7. Overall water production in option 1.

Parameters	SWRO	MSF	MSF-RO
Feed flowrate (m ³ /h)	3846.37	10,845.96	14,692.33
Production flowrate (m ³ /h)	2000	1000	3000
Blowdown flowrate (m ³ /h)	1846.38	9845.96	11,692.34
Water production ratio	0.52	0.09	0.20
Production concentration (kg/m ³)	0.20	0	0.13
Production temperature (°C)	25	33.23	27.74
Total price (CNY)	7012.21	7422.27	14,434.48
Unit price (CNY/m ³)	3.5061	7.4224	4.81

It can be seen from Table 7 that the water production ratio of the SWRO system is relatively high, at 0.52. The water production ratio of the MSF system is 0.092, and the water production ratio of the MSF-RO system is 0.2. It can be seen that the seawater utilization rate of the MSF system is low, and the water production ratio of the MSF-RO hybrid system is improved compared with the MSF system. At the same time, compared with the MSF system, the MSF-RO hybrid system reduces the unit price. Compared with the SWRO system, the produced water quality is improved.

4.1.2. The BR-MSF and SWRO System with Independent Feed Water

The simulation results of the SWRO and BR-MSF system costs in option 2 are shown in Tables 8 and 9. The total operating cost of the SWRO system is 7012.22 CNY, of which the operating energy consumption accounts for 65.13%. The unit price of SWRO system water production is 3.5061 CNY/m³. For the BR-MSF system, the total operating cost is 7397.14 CNY, of which the running energy consumption accounts for 26.81%. The unit price of BR-MSF water production is 7.3971 CNY/m³. Combining Tables 7 and 9, it can be seen that the unit price of BR-MSF water production in option 2 is lower than that of the

OT-MSF system in option 1. Therefore, the BR-MSF system is more energy efficient than the OT-MSF system to generate the same water resources.

Table 8. SWRO system cost ratio table.

Cost	Total Price (CNY)	Unit Price (CNY/m ³)	Proportion
OC_{IP}	378.98	0.1895	0.0540
OC_{CH}	903.90	0.4519	0.1289
OC_{EN}	4567.25	2.2836	0.6513
OC_{MER}	572.23	0.2861	0.0816
OC_{MN}	210.37	0.1052	0.0300
OC_{LB1}	333.33	0.1667	0.04754
OC_{WS1}	46.16	0.0231	0.0066
OC_{RO}	7012.22	3.5061	1

Table 9. BR-MSF system cost ratio table.

Cost	Total Price (CNY)	Unit Price (CNY/m ³)	Proportion
OC_{ST}	3285.80	3.2858	0.4442
OC_{EL}	1983.25	1.9832	0.2681
OC_{MT}	703.27	0.7033	0.0951
OC_{PR}	239.30	0.2393	0.0324
OC_{LB2}	888.02	0.8880	0.1200
OC_{WS2}	297.50	0.2975	0.0402
OC_{MSF}	7397.14	7.3971	1

It can be seen from Tables 7 and 10 that to produce the same volume of fresh water, the feed water flowrate of the BR-MSF system is 34.7% less than that of the OT-MSF system. So, the BR-MSF saves more water than OT-MSF. Moreover, the option 2 also improves the water production ratio of the simple MSF system, reduces the water production price of the MSF system and improves the water production quality of the SWRO system. Comparing the overall water production of options 1 and 2, it can be found that the water production ratio of option 2 is higher than that of option 1, because the water production economy of BR-MSF system is better than that of the OT-MSF system.

Table 10. Overall water production in option 2.

Parameters	SWRO	MSF	MSF-RO
Feed water flowrate (m ³ /h)	3846.37	7083.82	10,930.19
Production flowrate (m ³ /h)	2000	1000	3000
Blowdown flowrate (m ³ /h)	1846.38	11,900	13,746.38
Water production ratio	0.52	0.14	0.27
Production concentration (kg/m ³)	0.20	0	0.13
Production temperature (°C)	25	39.25	29.75
Total price (CNY)	7012.21	7397.14	14,409.35
Unit price (CNY/m ³)	3.5061	7.3971	4.8031

4.1.3. The Last-Stage Flash Water of the OT-MSF System as the Feed Water of the SWRO System

The cost simulation results of SWRO and OT-MSF systems in option 3 are shown in Tables 11 and 12. Comparing Tables 7 and 13, the water production cost of the SWRO and OT-MSF systems in option 3 is reduced by 120.3 m³/h and 92.66 m³/h. In options 1 and 3, the feed water flowrate of OT-MSF system is the same. In option 3, the feed water of the SWRO system is part of the wastewater from the OT-MSF system. Due to the high production temperature of the OT-MSF system, the permeation flux of the SWRO system is improved, so the feed water flowrate of the SWRO system of option 3 is lower

than that of the SWRO system of option 1. In addition, option 3 reduces the wastewater management cost of the OT-MSF system. It can be seen from Table 13 that the blowdown temperature of OT-MSF system is 33.23 °C, which is higher than the independent feed seawater temperature of the original SWRO system. Therefore, the permeation flux of SWRO system decreases, the water production ratio is improved, and the water production cost of the whole system is reduced.

Table 11. SWRO system cost ratio table.

Cost	Total Price (CNY)	Unit Price (CNY/m ³)	Proportion
OC_{IP}	365.19	0.1826	0.0530
OC_{CH}	871.00	0.4355	0.1264
OC_{EN}	4521.49	2.2607	0.6561
OC_{MER}	551.42	0.2757	0.0801
OC_{MN}	205.44	0.1027	0.0298
OC_{LB1}	333.40	0.1667	0.0484
OC_{WS1}	42.65	0.0213	0.0062
OC_{RO}	6891.91	3.4460	1

Table 12. BR-MSF system cost ratio table.

Cost	Total Price (CNY)	Unit Price (CNY/m ³)	Proportion
OC_{ST}	3193.96	3.1939	0.4358
OC_{EL}	2019.28	2.0193	0.2755
OC_{MT}	703.27	0.7033	0.0959
OC_{PR}	355.45	0.3555	0.0485
OC_{LB2}	904.15	0.9042	0.1234
OC_{WS2}	153.49	0.1535	0.0209
OC_{MSF}	7329.61	7.3296	1

Table 13. Overall water production in option 3.

Parameters	SWRO	MSF	MSF-RO
Feed flowrate (m ³ /h)	3706.40	10,845.96	14,552.36
Production flowrate (m ³ /h)	2000	1000	3000
Blowdown flowrate (m ³ /h)	1706.02	6139.56	7845.58
Water production ratio	0.54	0.09	0.21
Production concentration (kg/m ³)	0.20	0	0.13
Production temperature (°C)	33.23	33.23	33.23
Total price (CNY)	6891.91	7329.61	14,221.52
Unit price (CNY/m ³)	3.4460	7.3296	4.7405

4.1.4. The Last-Stage Flash Water of the BR-MSF System Is the Feed Water of the SWRO System

The cost-simulation results of SWRO and BR-MSF systems in option 4 are shown in Tables 14 and 15. It is found from Tables 10 and 16 that due to the use of the blowdown water with the heat of the BR-MSF system, the water production cost of SWRO and BR-MSF systems in option 4 is lower than that in option 2. It can be seen from Tables 13 and 16 that the water production ratio of the BR-MSF system is higher than that of the OT-MSF system. Therefore, the water production ratio of option 4 is also higher than that of option 3, and since the BR-MSF system is more economical in water production, the water production cost of option 4 is also reduced compared to option 3. It also can be seen from the conclusion of option 2. Based on the above data, compared with the above three options, option 4 is the best structure with the lower operational cost.

Table 14. SWRO system cost ratio table.

Cost	Total Price (CNY)	Unit Price (CNY/m ³)	Proportion
OC_{IP}	378.98	0.1895	0.0544
OC_{CH}	903.90	0.4519	0.1298
OC_{EN}	4567.25	2.2836	0.6558
OC_{MER}	572.23	0.2861	0.0822
OC_{MN}	208.94	0.1045	0.0300
OC_{LB1}	333.33	0.1667	0.0479
OC_{WS1}	0	0	0
OC_{RO}	6854.52	3.4273	1

Table 15. BR-MSF system cost ratio table.

Cost	Total Price (CNY)	Unit Price (CNY/m ³)	Proportion
OC_{ST}	3285.80	3.2858	0.4566
OC_{EL}	1983.25	1.9832	0.2756
OC_{MT}	703.27	0.7033	0.0977
OC_{PR}	239.30	0.2393	0.0333
OC_{LB2}	888.02	0.8880	0.1234
OC_{WS2}	96.17	0.0962	0.0134
OC_{MSF}	7195.81	7.1958	1

Table 16. Overall water production in option 4.

Parameters	SWRO	MSF	MSF-RO
Feed water flowrate (m ³ /h)	3663.14	7083.82	10,746.95
Production flowrate (m ³ /h)	2000	1000	3000
Blowdown flowrate (m ³ /h)	1663.03	3846.86	5509.89
Water production ratio	0.55	0.14	0.28
Production concentration (kg/m ³)	0.20	0	0.13
Production temperature (°C)	39.25	39.25	39.25
Total price (CNY)	6854.52	7195.81	14,050.33
Unit price (CNY/m ³)	3.4273	7.1958	4.6834

4.1.5. The Rejected Water of the BR-MSF System as the Feed Water of the SWRO System

In the option 5, rejected water in the BR-MSF system is used as the feed water of the SWRO system. The cost simulation results of SWRO and BR-MSF systems in option 5 are shown in Tables 17 and 18. The total operating cost of the SWRO system is 6833.22 CNY, of which the operating energy consumption accounts for 65.84%. The unit price of SWRO system water production is 3.4166 CNY/m³. For the BR-MSF system, the total operating cost is 7287.39 CNY, of which the running energy consumption accounts for 27.21%. The unit price of BR-MSF system water production is 7.2874 CNY/m³.

Table 17. SWRO system cost ratio table.

Cost	Total Price (CNY)	Unit Price (CNY/m ³)	Proportion
OC_{IP}	358.64	0.1793	0.0525
OC_{CH}	855.38	0.4277	0.1252
OC_{EN}	4498.86	2.2494	0.6584
OC_{MER}	541.01	0.2705	0.0792
OC_{MN}	205.00	0.1025	0.0300
OC_{LB1}	333.33	0.1667	0.0488
OC_{WS1}	41.00	0.0205	0.0060
OC_{RO}	6833.22	3.4166	1

Table 18. BR-MSF system cost ratio table.

Cost	Total Price (CNY)	Unit Price (CNY/m ³)	Proportion
OC_{ST}	3285.80	3.2858	0.4509
OC_{EL}	1983.25	1.9832	0.2721
OC_{MT}	703.27	0.7033	0.0965
OC_{PR}	239.30	0.2393	0.0328
OC_{LB2}	888.02	0.8880	0.1219
OC_{WS2}	187.75	0.1878	0.0258
OC_{MSF}	7287.39	7.2874	1

According to Table 19, compared with the above four options, option 5 has the highest water production temperature, reaching 42.25 °C. Option 5 uses the rejected water of the BR-MSF system as the feed water of the SWRO system. This option increases the temperature of the feed water of the SWRO system and improves the seawater utilization rate of the BR-MSF system. So, the unit price of the BR-MSF system is lower than that of option 2. However, compared with option 4, the total water production price of option 5 is 70.28 CNY higher than that of option 4. So, option 5 has insufficient economic advantages.

Table 19. Overall water production in option 5.

Parameters	SWRO	MSF	MSF-RO
Feed flowrate (m ³ /h)	3639.91	7083.81	10,723.73
Production flowrate (m ³ /h)	2000	1000	3000
Blowdown flowrate (m ³ /h)	1639.91	7510	9149.91
Water production ratio	0.55	0.14	0.28
Production concentration (kg/m ³)	0.20	0	0.13
Production temperature (°C)	44.96	37.43	42.45
Total price (CNY)	6833.22	7287.39	14,120.61
Unit price (CNY/m ³)	3.4166	7.2874	4.7069

4.1.6. The Rejected Water of the SWRO System as Part of the Feed Water of the OT-MSF System

Differently from options 3, 4, and 5, in option 6, seawater and part of blowdown in the SWRO system are used as feed water of the OT-MSF system. The cost simulation results of SWRO and OT-MSF systems are shown in Tables 20 and 21. The total operating cost of the SWRO system is 6964.63 CNY, of which the operating energy consumption accounts for 65.58%. The unit price of SWRO system water production is 3.4823 CNY/m³. For the OT-MSF system, the total operating cost is 7266.67 CNY, of which the running energy consumption accounts for 27.28%. The unit price of SWRO system water production is 7.2667 CNY/m³.

Table 20. SWRO system cost ratio table.

Cost	Total Price (CNY)	Unit Price (CNY/m ³)	Proportion
OC_{IP}	378.98	0.1895	0.0544
OC_{CH}	903.90	0.4519	0.1298
OC_{EN}	4567.25	2.2836	0.6558
OC_{MER}	572.23	0.2861	0.0822
OC_{MN}	208.94	0.1045	0.0300
OC_{LB1}	333.33	0.1667	0.0479
OC_{WS1}	0	0	0
OC_{RO}	6964.63	3.4823	1

Table 21. OT-MSF system cost ratio table.

Cost	Total Price (CNY)	Unit Price (CNY/m ³)	Proportion
OC_{ST}	3193.96	3.1940	0.4395
OC_{EL}	1982.44	1.9824	0.2728
OC_{MT}	703.27	0.7033	0.0968
OC_{PR}	236.70	0.2367	0.0326
OC_{LB2}	904.15	0.9042	0.1244
OC_{WS2}	246.15	0.2461	0.0339
OC_{MSF}	7266.67	7.2667	1

According to Table 19, option 6 uses the rejected water of the SWRO system as part of the feed water of the OT-MSF system, which saves the feed water of the OT-MSF system, comprehensively improves the quality of the water produced by the SWRO system, and reduces the amount of blowdown. Compared with option 2, the total price of water production in this option is reduced, and the water production ratio is reduced. This option is more economical than the option 2 system. This is because the water production by the SWRO system is reprocessed by the OT-MSF system, which reduces the cost of the entire system. However, compared with option 3, the total water production price of this option is higher. Because option 3 utilizes the waste heat of the OT-MSF system, the utilization rate of water resources is improved. Based on the comparison of other options, the advantages of option 6 are not outstanding.

4.1.7. The Rejected Water of SWRO System as Part of the Feed Water of BR-MSF System

In option 7, the seawater and part of blowdown in the SWRO system are used as the feed water of BR-MSF system, which saves the feed water of BR-MSF system, comprehensively improves the water production quality of SWRO system and reduces the blowdown. The simulation results are shown in Tables 22 and 23, and the water production of the hybrid system is shown in Table 24. According to comprehensive Tables 24 and 25, the unit price of SWRO system water production in options 6 and 7 are the same, both being 3.4823 CNY/m³. Due to the economic advantages of the BR-MSF system in water production, option 7 has lower water production price than option 6, but compared with option 4, the economic advantages are insufficient. Because option 4 utilizes the waste heat of the BR-MSF system, the utilization rate of water resources is improved.

Table 22. SWRO system cost ratio table.

Cost	Total Price (CNY)	Unit Price (CNY/m ³)	Proportion
OC_{IP}	378.98	0.1895	0.0544
OC_{CH}	903.90	0.4519	0.1298
OC_{EN}	4567.25	2.2836	0.6558
OC_{MER}	572.23	0.2861	0.0822
OC_{MN}	208.94	0.1045	0.0300
OC_{LB1}	333.33	0.1667	0.0479
OC_{WS1}	0	0	0
OC_{RO}	6964.63	3.4823	1

Table 23. OT-MSF system cost ratio table.

Cost	Total Price (CNY)	Unit Price (CNY/m ³)	Proportion
OC_{ST}	3285.80	3.2858	0.4537
OC_{EL}	1946.41	1.9464	0.2688
OC_{MT}	703.27	0.7033	0.0971
OC_{PR}	120.54	0.1205	0.0166
OC_{LB2}	888.02	0.8880	0.1226
OC_{WS2}	297.50	0.2975	0.0411
OC_{MSF}	7241.54	7.2415	1

Table 24. Overall water production in option 4.

Parameters	SWRO	MSF	MSF-RO
Feed water flowrate (m ³ /h)	3846.37	5237.43	9083.81
Production flowrate (m ³ /h)	2000	1000	3000
Blowdown flowrate (m ³ /h)	0	11,900	11,900
Water production ratio	0.52	0.14	0.33
Production concentration (kg/m ³)	0.20	0	0.13
Production temperature (°C)	25	39.25	29.75
Total price (CNY)	6964.63	7241.54	14,206.17
Unit price (CNY/m ³)	3.4823	7.2415	4.7354

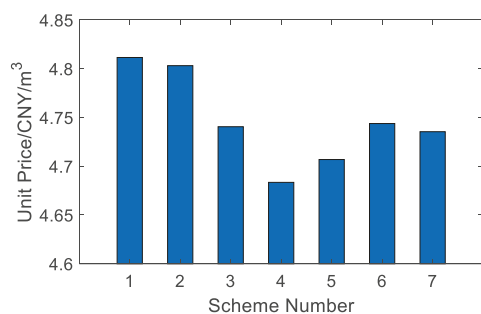
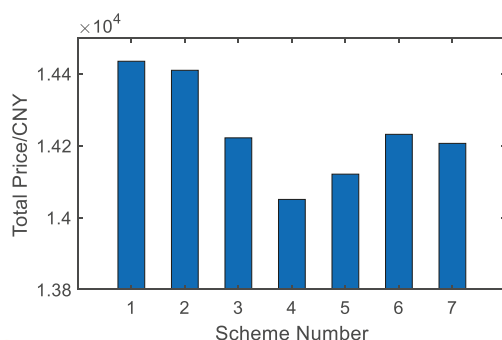
Table 25. Overall water production in option 6.

Parameters	SWRO	MSF	MSF-RO
Feed water flowrate (m ³ /h)	3846.37	6999.59	10,845.96
Production flowrate (m ³ /h)	2000	1000	3000
Blowdown flowrate (m ³ /h)	0	9845.96	9845.96
Water production ratio	0.52	0.09	0.28
Production concentration (kg/m ³)	0.20	0	0.13
Production temperature (°C)	25	33.23	27.74
Total price (CNY)	6964.63	7266.67	14,231.30
Unit price (CNY/m ³)	3.4823	7.2667	4.7438

4.2. Evaluation of System Economics and Water Production Performance

4.2.1. System Water Production Cost Evaluation

As shown in Figures 10 and 11, among the seven options, option 4 has the lowest water production price at 4.6834 CNY/m³, and option 1 has the highest water production price at 4.8115 CNY/m³. Option 4 is that the last-stage flash water from the BR-MSF system is used as the feed water of the SWRO system, which saves a lot of wastewater management costs of the BR-MSF system. Although the unit price advantage of system water production is not obvious, the total price of system water production is quite different.

**Figure 10.** Comparison of unit price.**Figure 11.** Comparison of total price.

4.2.2. System Blowdown Flowrate Evaluation

As shown in Figure 12, among the seven options, option 4 has the lowest blowdown flowrate, with a blowdown flowrate of $5509.89 \text{ m}^3/\text{h}$. Consistent with the comparison of system water prices, option 4 has an advantage in terms of system water price because of its blowdown flowrate.

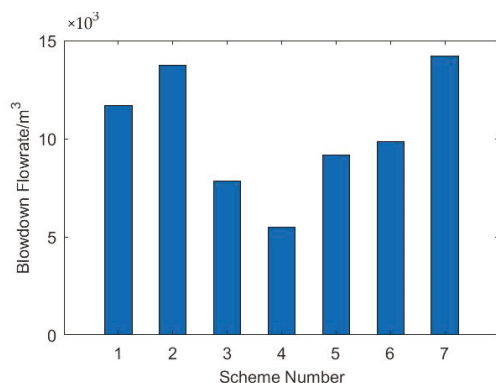


Figure 12. Comparison of blowdown flowrate.

4.2.3. System Water Production Ratio Evaluation

As shown in Figure 13, in the seven options, the water production ratio is almost the same, and the difference is not obvious. In comparison, option 7 has the highest water production ratio because all wastewater of the SWRO system flows into the BR-MSF system, which improves the overall water production ratio of the system. Comparing option 1 and option 2; option 3 and option 4; and option 6 and option 7—when the MSF hybrid system is the BR-MSF system, the corresponding option has more advantages in the comparison of water production ratio.

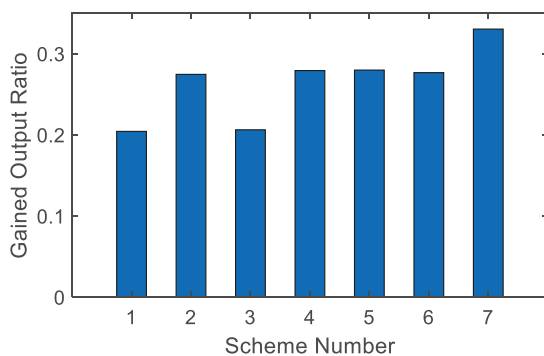


Figure 13. Comparison of water production ratio.

4.2.4. System Water Production Temperature Evaluation

As shown in Figure 14, among the seven options, option 5 has the highest water production temperature, followed by option 4. The water temperature of the SWRO system depends entirely on the influence of the feed temperature. In the option 5, the condensed water of the BR-MSF system in the coupling system is used as the feed water of the SWRO, which increases the water temperature of the SWRO system and comprehensively increases the water temperature of the entire option. In options 1, 2, 6, and 7, the temperature of the SWRO system is completely affected by the seawater temperature, so the water produced in the overall system is different from those in options 3, 4, and 5.

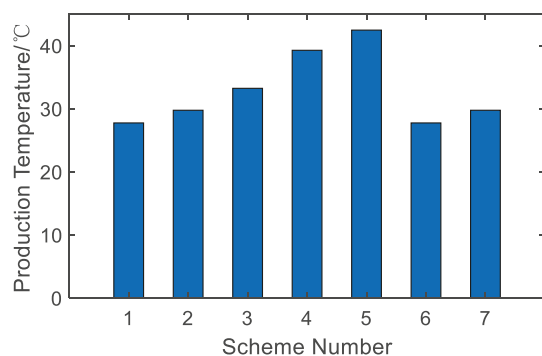


Figure 14. Comparison of production temperature.

4.2.5. Comprehensive Evaluation

As shown in Table 26, based on the systematic evaluation of the above four aspects, the seven hybrid options are comprehensively ranked in terms of water production price, blow-down flowrate, water production ratio, and production temperature. The four evaluation indexes are ranked by the advantages of low price, low flowrate, high water production ratio, and high temperature.

Table 26. Number of variables with IDM.

Rankin	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7
Index							
Price	Option 4	Option 5	Option 7	Option 3	Option 6	Option 2	Option 1
Blowdown	Option 4	Option 3	Option 5	Option 6	Option 1	Option 7	Option 2
Gained output ratio	Option 7	Option 5	Option 4	Option 6	Option 2	Option 3	Option 1
Production temperature	Option 5	Option 4	Option 3	Option 7	Option 2	Option 6	Option 1

It can be seen from the results that option 4 ranks first among the seven options in terms of price and blowdown flowrate, and remains in the forefront in terms of water-making ratio. However, there is little difference between options 5 and 4 in terms of water-making ratio. Overall, option 4 has certain advantages and performs well in the four evaluation indexes. For the option 1 and option 2, they all rank last in the four evaluation indexes, with obvious disadvantages. The above results provide guidance for the feeding conditions of the MSF-RO system, and provide a certain basis for the subsequent optimization of system operation and the complexity of the hybrid option.

5. Conclusions

In addition to combining a new energy-driven system with RO or MSF seawater desalination to achieve better economic and social benefits, studies of better combinations of MSF-RO systems to obtain more techno-economic profits are also very attractive. In this work, based on the mechanism models of RO and MSF processes, modeling and structural optimization of hybrid MSF-RO system is carried out with the consideration of seven coupled structures. The feeding, discharging, and mixing separation modules of the system are modeled and the operational economics, the evaluation indexed are built. Simulation and calculation of the hybrid system with the seven coupled structures leading to the profiles of techno-economic performance as well as specific state values. The results show that: the fourth structural option has the lowest operational cost with the value of 4.6834 CNY/m³, which is obviously better than the other options. In addition, the fourth structural option can achieve the lowest wastewater blowdown. For minimizing the index of gained output ratio and production temperature, the seventh and the fifth option rank the first. More than that, from the numerical simulation and analysis, the evaluation index of the production price, blowdown flowrate, water production ratio, and water production temperature can all be obtained as well as those important state variables.

Our work is helpful for the optimal operation and design of the MSF-RO system with detailed model-based numerical calculation. In the future work, more case studies for real plant application and the optimal control will be focused.

Author Contributions: Conceptualization, L.H.; methodology, Q.H. and A.J.; validation, J.W. and C.L.; investigation, Y.Z. and Y.X.; writing—original draft preparation, L.H. and Q.H.; writing—review and editing, A.J. and C.L.; supervision, Y.X. and J.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Zhejiang Provincial Natural Science Foundation, grant number LY20F030010, and the National Natural Science Foundation of China, grant number 61973102.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

a	decay level of water permeability
A_w	membrane water permeability ($\text{m}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$)
A_{w0}	intrinsic membrane water permeability ($\text{m}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$)
b	decay level of TDS permeability
B_s	membrane TDS permeability (m/s)
B_{s0}	intrinsic membrane TDS permeability (m/s)
C_b	bulk concentration along feed channel (kg/m^3)
C_f	feed salt concentration (kg/m^3)
C_m	salt concentration of membrane surface (kg/m^3)
C_p	permeate concentration of RO unit (kg/m^3)
C_r	brine concentration (kg/m^3)
C_{sp}	permeate concentration of permeate side (kg/m^3)
FA	irreversible degradation coefficient of A_w
FB	irreversible degradation coefficient of B_s
J_v	solvent flux ($\text{kg}/\text{m}^2\cdot\text{s}$)
J_s	solute flux ($\text{kg}/\text{m}^2\cdot\text{s}$)
L	length of the RO channel (m)
MFA	membrane performance coefficient of A_w
MFB	membrane performance coefficient of B_s
MOD	number of membrane module
Ncl	cleaning frequency
n_l	number of leaves in RO module
n_{pv}	number of pressure vessel
OC	operational cost of whole process
OC_{EN}	energy cost of RO process
OC_{BP}	energy cost of boost pump
OC_{CH}	cost for chemicals
OC_{IP}	energy cost for intake and pretreatment
OC_{ME}	cost for membrane replacement
OC_{MN}	cost for system maintenance
OC_{MNCON}	cost for conventional equipment maintenance
OC_{MNCL}	cost for membrane module cleaning
OC_{OT}	membrane cleaning cost for chemicals
OC_{PC}	membrane cleaning cost for other
P_b	pressure along feed channel (bar)
P_{elc}	electricity price
P_d	pressure drop along RO spiral wound module (bar)

P_f	feed pressure (bar)
P_p	pressure in permeate side (bar)
P_r	brine pressure (bar)
P_{ri}	membrane price
PLF	load coefficient
Q_f	feed flowrate (m ³ /h)
Q_p	permeate flowrate (m ³ /h)
Q_r	brine flowrate (m ³ /h)
WR	water recovery ratio
SR	salt rejection coefficient (%)
SEC	specific energy consumption (kw·h/m ³)
t	operation time of membrane module (day)
t_q	membrane operation time after last cleaning
T	feed (operational) temperature (K)
V_b	axial velocity of bulk flow (m/s)
V_f	axial velocity of feed flow (m/s)
V_r	axial velocity of brine flow (m/s)
W	width of the RO module (m)
X_{cl}	membrane cleaning time
X_{mr}	membrane replacing time
$\alpha_1, \alpha_2, \beta_1$	constant parameters
$\Delta\pi$	pressure loss of osmosis pressure (bar)
ΔT	time of each schedule period
ΔT_{cl}	membrane use time since last cleaning
ρ	density of permeate water (kg/m ³)
λ	friction factor
ζ	membrane replacing rate
ε_p	mechanical efficiency of high-pressure pump
ε_{pf}	energy recovery efficiency
b	bulk
f	module feed channel
m	membrane surface
p	permeate side
r	brine side

References

1. Khawaji, A.D.; Kutubkhanah, I.K.; Wie, J.M. Advances in seawater desalination technologies. *Desalination* **2008**, *221*, 47–69. [CrossRef]
2. Tu, S.; Deng, S.; Wang, X. The 6th World Water Forum issued a proposal to the world—Water management and water development. *China Water Resour.* **2012**, *6*, 11–15.
3. Qiu, M. Brief Analysis of Seawater Desalination Technology in my country. *China Environ. Prot. Ind.* **2018**, *3*, 58–60.
4. Gao, C.; Ruan, G. *Seawater Desalination Technology and Engineering*; Chemical Industry Press: Beijing, China, 2004; pp. 1–2.
5. Manesh, M.H.K.; Kabiri, S.; Yazdi, M. Exergoenvironmental analysis and evaluation of coupling MSF, MED and RO desalination plants with a combined cycle plant. *Int. J. Exergy* **2020**, *33*, 76–97. [CrossRef]
6. Fan, Z.; Li, Y.; Wang, X. Current Situation and Prospects of Thermal Film Coupling Seawater Desalination Technology. *Power Stn. Aux. Equip.* **2013**, *34*, 9–12.
7. Wazeera, I.; Khanb, S.U.D.; Al-Mutaza, I.S.; AlAteeq, T.M.; Chafidz, A.; Khan, S.U. Assessment of the design, operation, and economy of the seawater reverse osmosis plant in Al-Jubail region, Saudi Arabia. *Desalination Water Treat.* **2021**, *222*, 60–80. [CrossRef]
8. Khan, S.U.D.; Orfi, J. Socio-Economic and Environmental Impact of Nuclear Desalination. *Water* **2021**, *13*, 1637. [CrossRef]
9. Kuenstle, K.; Moricet, M.; Marquardt, K.; Nagel, R. Conceptual design and economical evaluation of a combined MSF-RO seawater desalination plant. *Desalination* **1983**, *44*, 61–72. [CrossRef]
10. Al-Marafie, A.M.R. Prospects of hybrid RO-MSF desalting plants in Kuwait. *Desalination* **1989**, *72*, 395–404. [CrossRef]
11. Awerbuch, L.; Mast, V.; Soo-Hoo, R. Hybrid desalting systems—A new alternative. *Desalination* **1987**, *64*, 51–63. [CrossRef]
12. Awerbuch, L.; May, S.; Soo-Hoo, R.; Mast, V. Hybrid desalting systems. *Desalination* **1989**, *64*, 51–63. [CrossRef]
13. Al-Mutaz, I.S.; Soliman, M.A.; Daghtem, A.M. Optimum design for a hybrid desalting plant. *Desalination* **1989**, *72*, 395–404. [CrossRef]

14. El-Sayed, E.; Ebrahim, S.; Al-Saffar, A.; Abdel-Jawad, M. Pilot study of MSF/RO hybrid systems. *Desalination* **1998**, *120*, 121–128. [CrossRef]
15. Cardona, E.; Culotta, S.; Piacentino, A. Energy saving with MSF-RO series desalination plants. *Desalination* **2002**, *153*, 167–171. [CrossRef]
16. Helal, A.M.; El-Nashar, A.M.; Al-Katheeri, E.; Al-Malek, S. Optimal design of hybrid RO/MSF desalination plants part I: Modeling and algorithms. *Desalination* **2003**, *154*, 43–66. [CrossRef]
17. Helal, A.M.; El-Nashar, A.M.; Al-Katheeri, E.; Al-Malek, S. Optimal design of hybrid RO/MSF desalination plants part II: Results and discussions. *Desalination* **2004**, *160*, 13–27. [CrossRef]
18. Helal, A.M.; El-Nashar, A.M.; Al-Katheeri, E.; Al-Malek, S. Optimal design of hybrid RO/MSF desalination plants part III: Sensitivity analysis. *Desalination* **2004**, *169*, 43–60. [CrossRef]
19. Marcovecchio, M.G.; Mussati, S.F.; Aguirre, P.A.; Scenna, N.J. Optimization of hybrid desalination processes including multi stage flash and reverse osmosis systems. *Desalination* **2005**, *182*, 111–122. [CrossRef]
20. Vince, F.; Marechal, F.; Breant, P.; Aoustin, E. Innovative Design and Multi-Objective Optimization of Hybrid Reverse Osmosis and Multi-Stage Flash Desalination Plants. In Proceedings of the Conference on CHISA 2006-17th International Congress of Chemical and Process Engineering, Prague, Czech Republic, 27–31 August 2006; pp. 56–61.
21. Abdulrahim, H.K.; Hassan, K.; Alasfour, F.N. Multi-objective optimisation of hybrid MSF-RO desalination system using genetic algorithm. *Int. J. Exergy* **2010**, *7*, 387–424. [CrossRef]
22. Wu, L.; Xiao, S.; Hu, Y.; Gao, C. Optimal design of coupled seawater desalination system. *J. Chem. Ind. Eng.* **2012**, *63*, 3574–3578.
23. Malik, S.N.; Bahri, P.A.; Vu, L. Superstructure Development, Simulation and Optimization of Desalination Systems using Aspen Custom Modeler. In Proceedings of the 12th International Symposium on Process Systems Engineering and 25th European Symposium on Computer Aided Process Engineering, Copenhagen, Denmark, 31 May–4 June 2015; pp. 383–388.
24. Bloushi, A. *Environmental Impact and Technoeconomic Analysis of Hybrid MSF/RO Desalination: The Case Study of Al Taweelah A2 Plant*; Khalifa University of Science and Technology: Abu Dhabi, United Arab Emirates, 2018.
25. Bandi, C.S.; Uppaluri, R.; Kumar, A. Global optimality of hybrid MSF-RO seawater desalination processes. *Desalination* **2016**, *400*, 47–59. [CrossRef]
26. Hawaidi, E.A.M.; Mujtaba, I.M. Simulation and optimization of MSF desalination process for fixed freshwater demand: Impact of brine heater fouling. *Chem. Eng. J.* **2010**, *165*, 545–553. [CrossRef]
27. Tanvir, M.S.; Mujtaba, I.M. Optimisation of design and operation of MSF desalination process using MINLP technique in gPROMS. *Desalination* **2008**, *222*, 419–430. [CrossRef]
28. Alsadaie, S.M.; Mujtaba, I.M. Generic Model Control (GMC) in Multistage Flash (MSF) Desalination. *J. Process Control.* **2016**, *44*, 92–105. [CrossRef]
29. Woldai, A. *Multi-Stage Flash Desalination: Modeling, Simulation, and Adaptive Control*; CRC Press: London, UK, 2016; pp. 27–30.
30. Rosso, M.; Beltramini, A.; Mazzotti, M. Modeling multistage flash desalination plants. *Desalination* **1997**, *108*, 365–374. [CrossRef]
31. Gao, H.; Jiang, A.; Huang, Q.; Xia, Y.; Gao, F.; Wang, J. Mode-Based Analysis and Optimal Operation of MSF Desalination System. *Processes* **2020**, *8*, 794. [CrossRef]
32. Jiang, A.; Wang, H.; Lin, Y.; Cheng, W.; Wang, J. A study on optimal schedule of membrane cleaning and replacement for spiral-wound SWRO system. *Desalination* **2017**, *404*, 259–269. [CrossRef]
33. Jiang, A.; Biegler, L.T.; Wang, J.; Cheng, W.; Ding, Q.; Jiang, Z. Optimal operations for large-scale seawater reverse osmosis networks. *J. Membr. Sci.* **2015**, *476*, 508–524. [CrossRef]
34. Jiang, A.; Wang, J.; Biegler, L.T.; Cheng, W.; Xing, C.; Jiang, Z. Operational cost optimization of a full-scale SWRO system under multi-parameter variable conditions. *Desalination* **2015**, *355*, 124–140. [CrossRef]
35. Ma, R.; Zhang, P.; Sun, W.; Nie, G.; Li, W. Improvement of reverse osmosis membrane fouling prediction model. *Environ. Prot. Chem. Ind.* **2012**, *32*, 133–136.
36. Cheng, W. *Optimization Research of Large-Scale Reverse Osmosis Seawater Desalination System*; Hangzhou Dianzi University: Hangzhou, China, 2016.
37. Wade, N.M. Distillation plant development and cost update. *Desalination* **2001**, *136*, 3–12. [CrossRef]
38. He, L.; Xia, Y.; Li, C.; Jiang, A.; Zhao, Y.; Xie, F. Simulation and Operational Optimization of RO Based Desalination for Coal-Fired Power Plants' Wastewater. *Membranes* **2022**, *12*, 478. [CrossRef]
39. Fan, X.; Zhang, W. Technical and Economic Comparison of Membrane Process and Distillation Process for Seawater Desalination. *Electr. Equip.* **2007**, *7*, 44–47.



Article

Simulation and Operational Optimization of RO Based Desalination for Coal-Fired Power Plants' Wastewater

Lu He ¹, Yudong Xia ¹, Chuang Li ¹, Aipeng Jiang ^{1,*}, Yan Zhao ² and Fengling Xie ¹

¹ School of Automation, Hangzhou Dianzi University, Hangzhou 310018, China; 202060285@hdu.edu.cn (L.H.); 42072@hdu.edu.cn (Y.X.); lichuang_1006@163.com (C.L.); 211060052@hdu.edu.cn (F.X.)

² Chn Energy Lucency Enviro-Tech Co., Ltd., Beijing 100039, China; 12030975@chnenergy.com.cn

* Correspondence: jiangaipeng@hdu.edu.cn; Tel.: +86-0571-8691-9133

Abstract: Focusing on the problems of opaqueness and high energy consumption in coal-fired power plant wastewater recycling processes, this paper studies the simulation and operational optimization of coal-fired power plant wastewater treatment by taking a coal-fired power plant system in Inner Mongolia as an example. Firstly, based on the solution–diffusion theory, pressure drop, and osmotic concentration polarization, a mechanistic model equation for coal-fired power plant wastewater treatment is developed. Secondly, the equation fitness and equation parameters are calibrated to obtain an accurate model. Thirdly, the system is simulated and analyzed so as to obtain the influence and change trajectories of different feed flowrates, temperatures, pressures, and concentrations on various aspects of the system's performance, such as water recovery rate, salt rejection rate, and so on. Finally, in order to reduce the operating cost of the system, an optimization analysis is carried out, with the lowest specific energy consumption and average daily operating cost as optimization goals, and the performance changes of the system before and after optimization under three different working conditions are compared. The results show that adopting the given optimal strategy can significantly reduce the system's operational cost. This research is helpful for the digitization and low-carbon operation of coal-fired power plant wastewater treatment systems.

Keywords: coal-fired power plant wastewater; membrane; simulation; optimization; mechanistic model

1. Introduction

With the advancement of industrialization and urbanization, the discharge of wastewater has become increasingly uncontrolled, resulting in a series of environmental problems and a global water shortage. As water usage is a key operational aspect of most industrial processes, the generation of a large amount of industrial wastewater is inevitable [1,2]. With the significant increase in the world's energy consumption, in order to meet the demand for increasing electricity consumption, coal-fired power plants have been intensively utilized [3]. Water is an essential and fundamental resource in thermal power plants with various uses: as a make-up for boiler feed water, in the cooling of bearings and equipment, and in various plant services. Nowadays, China has formed a coal-based energy production structure with oil, natural gas, electricity, and other energies complementing each other. Coal-based electricity accounts for about 90% of energy production [4]. Therefore, a large amount of water is used in coal-fired power plants in China. It has become very important to treat and reuse the wastewater from coal-fired power plants, especially in Central and Western China, due to water shortages.

Compared with seawater, wastewater from coal-fired power plants has a high pH and COD (chemical oxygen demand) and a complex water quality, which make treatment and reuse very difficult [5]. Coal-fired power plants' wastewater is mainly divided into two categories: saline wastewater and organic wastewater [6]. Saline wastewater comes from

recycling systems, such as circulating water systems and chemical water station drainage, mainly containing inorganic salts, such as Cl^- , SO_4^{2-} , Na^+ , and Ca^{2+} . Based on TDS, it can be classified into low-saline and high-salt water. The TDS of low-saline water is usually less than 10,000 mg/L and that of high-salt water is usually 10,000~20,000 mg/L. The organic wastewater produced by coal-fired power plants comes from gasification process wastewater, coal-water slurry, and black water of dry coal-pulverized entrained flow gasification, etc. It mainly contains phenol, naphthalene, anthracene, and thiophene. These are all refractory organics with poor biodegradability and are highly difficult to treat, requiring biochemical treatment. Saline water makes up a large share of wastewater in coal-fired power plants, and thus more efforts should be made to desalinate and reuse the wastewater.

So far, the desalination methods for saline wastewater treatment from coal-fired power plants mainly include membrane technology and thermal technology. Among them, membrane technology mainly includes microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), etc. Thermal technology mainly includes multi-stage flash (MSF), multiple effect distillation (MED), and vapor compression (VC), etc. [7–9]. Reverse osmosis (RO) technology is extensively adopted in the treatment of wastewater from coal-fired power plants due to the advantages of high efficiency, simple operation, and maintenance of biological activity [10,11]. However, the operational efficiency of RO-based desalination systems is greatly affected by the feeding conditions of wastewater [12]. Therefore, it is of great significance to study the inherent operating characteristics of RO-based wastewater desalination systems so as to take effective measures to reduce the energy consumption and operational costs of these systems. For this reason, a mechanistic model is required to simulate and study the RO-based desalination process, at the same time enabling the operational optimization of the process.

Reverse osmosis seawater (SWRO) desalination is a typical resource treatment method of concentrated brine desalination. Malek et al. [13] established a model of a large-scale seawater desalination plant, including seawater intake and a pretreatment model, a high-pressure pump model, an energy recovery system model, and an RO process model. Based on these models, a replacement plan for membrane elements, system investment cost, and operating cost were provided, and an economic analysis was also carried out. Based on the solution–diffusion theory, Al-Bastaki et al. [14] established a mechanistic model of hollow fiber RO membranes, which considered the effects of pressure drops and concentration polarization. Considering the complex spatiotemporal variability of the membrane modules in the RO process, Karabelas et al. [15] proposed a “scale separation” global structured modeling method to develop a comprehensive SWRO system model. Al-Enezi et al. [16] gave the main structure of the RO system, which mainly includes one-stage, two-stage, and two-pass RO devices, and analyzed the effect of feed concentration and temperature on the salt rejection rate of the RO system. Oh et al. [17] gave a system model of SWRO based on solution–diffusion theory and studied the relationship between recovery rate and permeate flux and other performance aspects of the RO system. Kaghazchi et al. [18] presented an RO system mechanistic model of two desalination plants in the Persian Gulf region and analyzed the influence of operating parameters on system performance. Lu et al. [19] established a mathematical model of the desalination process unit, predicted the impact of operating parameters on the RO process under different conditions through simulation analysis, and gave the relevant economic model.

Using a detailed mathematical model of the RO-based desalination process, the optimized operation could be obtained by solving its corresponding optimization problem. In 2005, Marcovecchio et al. [20] established the mechanistic model of the hollow fiber membrane system and the economic model of the RO system, discretized the model by using the PR algorithm, and finally solved the optimization problem by GAMS. In 2007, Luo et al. [21] used the average value of the parameters of the membrane element model simplification of the differential solution operation. In 2013, Kim et al. [22] transformed the implicit mathematical model of the desalination process into an explicit model by converting the

exponential function into a second-order polynomial and tested the accuracy, rapidity, and robustness of this method. In 2017, Gong et al. [23] used the finite element configuration method to discretize the differential equations in the membrane RO process model and optimized the solution by GAMS. In 2021, Blechschmidt et al. [24] used neural networks to solve the differential equations; this method is significant for RO system performance research.

In addition to using mechanistic modeling to analyze the RO process, some researchers have proposed a new method in recent years. In 2021, Cai et al. [25] used artificial neural network (ANN) and multilinear regression (MLR) techniques to model industrial RO concentrate processing. The performance of the models in predicting total organic carbon removal and sludge production in reverse osmosis concentrate treatment was evaluated and the ANN model's predictive accuracy was validated. In 2021, Wang et al. [26] developed an ion transport model for RO, referred to as the solution–friction model, by rigorously considering the mechanisms of partitioning and the interactions among water, salt ions, and the membrane. Ion transport through the membrane is described by the extended Nernst–Planck equation, with the consideration of frictions between species. The model is validated using experimental measurements of salt rejection and permeate water flux in a lab-scale, cross-flow RO setup. Lastly, the pressure drop distribution across the membrane was analyzed by means of a framework. Bonny et al. [27] suggested a novel and efficient approach to determining transmembrane pressure using Deep Reinforcement Learning (DRL) and used a Deep Deterministic Policy Gradient (DDPG) agent to adjust the pressure across a membrane.

The above studies provide strong support for the modeling and solution of the RO process of membrane desalination, but most studies are mainly aimed at the desalination process of seawater or specific brines. It is known that there are few studies on modeling the wastewater treatment process of coal-fired power plants. Cai, Bonny, Salgado-Reyna, and Al-Obaidi et al. [25,27–29] used intelligent algorithms to model and analyze the RO process. These excellent studies used intelligent algorithms for research analysis; unfortunately, there may be some uncertainty in the analytic process. In this study, a mechanistic modeling method is applied to the treatment of coal-fired power plant wastewater so that the internal operation of the RO membrane can be seen intuitively. Most studies which establish mechanistic modeling are mainly aimed at the desalination process of seawater or specific brines, and there are few studies on the treatment of coal-fired power plant wastewater. Hence, a further improvement of the above models is required before they can be used for the simulation and operational optimization of the membrane treatment process of coal-fired power plant wastewater. Similarly, this study of coal-fired power plant wastewater treatment is relevant to the study of actual plants.

Therefore, in order to realize the efficient operation of coal-fired power plant wastewater treatment processes, this paper establishes a mechanistic model of an RO-based desalination system for coal-fired power plant wastewater treatment based on the theory of dissolution and diffusion, energy conservation, and material conservation. Then, aiming at the mismatch of model parameters, the parameters of the model are identified to obtain an accurate coal-fired power plant wastewater membrane treatment process model. Finally, the whole process is simulated and optimized to obtain the production process state and to determine mutual influence relationships, as well as the optimal operation strategy, so as to realize the optimal operation of the production process for the membrane treatment of coal-fired power plant wastewater.

2. Process Flow of Coal-Fired Power Plant Wastewater

RO modules are mainly divided into two types: spiral wound RO modules and hollow fiber RO modules. Compared with the hollow fiber RO module, the spiral wound RO module has a more compact structure and a larger effective membrane area per unit volume, so the spiral wound RO module is more popular [30]. Hence, this paper will analyze the

spiral wound RO module. The process flow of a typical “zero-emission” coal-fired power plant wastewater treatment system is shown in Figure 1.

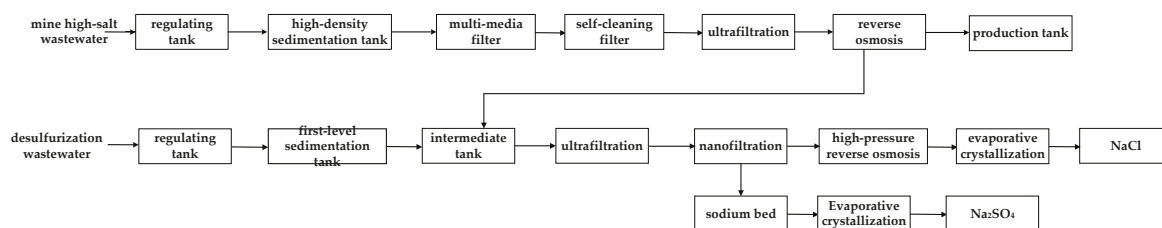


Figure 1. Typical process flow of coal-fired power plant wastewater.

It can be seen from Figure 1 that the coal-fired power plant wastewater process mainly treats mine high-salt wastewater and desulfurization wastewater. The main process is as follows: the high-salt wastewater of the mine is extracted from the mine by the high-pressure pump and the impurities in the wastewater are removed by flocculation in the regulating tank; subsequently, the mine wastewater enters the high-density sedimentation tank. After dosing treatment, the wastewater passes through the multi-media filter, the self-cleaning filter, and ultrafiltration to remove other impurities. Then, it enters the RO modules to obtain fresh water and concentrated brine; after that the fresh water enters the RO production tank for further conditioning to become usable water and the concentrated brine enters the intermediate tank of the desulfurization wastewater process for further treatment. The desulfurization wastewater treatment process removes impurities through the adjustment tank and the first-level sedimentation tank and then the wastewater enters the intermediate tank. The intermediate tank mixes the concentrated brine produced by the mine’s high-salt wastewater process. The desulfurization wastewater is treated by ultrafiltration, nanofiltration, and high-pressure reverse osmosis. Finally, the desulfurization wastewater is evaporated and crystallized to obtain NaCl and NaSO₄, realizing the “zero-emission” treatment of coal-fired power plant wastewater.

With respect to the above process, this paper only analyzes the RO module in the mine high-brine treatment process. The arrangements of RO membranes in common RO modules mainly include one-stage, multi-stage, and multi-pass RO systems. This paper studies and analyzes the RO device with a two-stage system, and its flow chart is shown in Figure 2. After a series of treatments, the high-salt wastewater enters the RO device module and after the high-pressure pump pressurizes the high-salt water is pressed into the first-stage RO membrane for treatment to produce fresh water and concentrated brine water. The concentrated brine enters the second-stage RO membrane through the booster pump for treatment. In the same way, fresh water and concentrated brine can be obtained. The fresh water produced from the two stages enters the RO production tank and the concentrated brine enters the desulfurization wastewater treatment process and is treated again to realize the resource utilization of coal-fired power plant wastewater. The first-stage RO module consists of 12 pressure vessels; the second-stage RO module consists of 7 pressure vessels. Six membranes are connected in series in each pressure vessel.

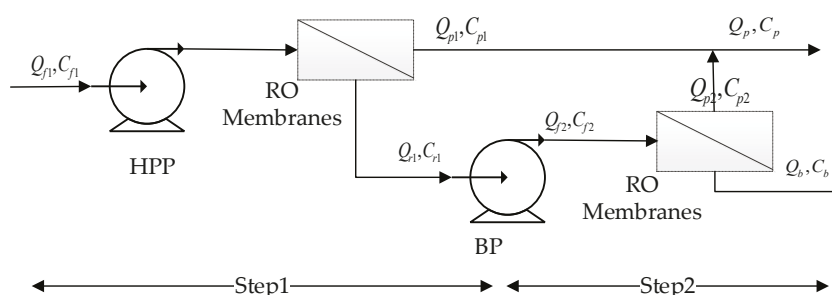


Figure 2. Flow chart of a two-stage RO plant.

3. Modeling of the RO Process of Coal-Fired Power Plant Wastewater Treatment

Figure 3 shows the internal schematic diagram of the feed channel of spiral wound RO modules [12,18,31,32]. The feed water passes through the membrane channel to obtain fresh water and concentrated brine, respectively. The complete two-stage RO process mathematical model includes a process transport model and a system model [33,34].

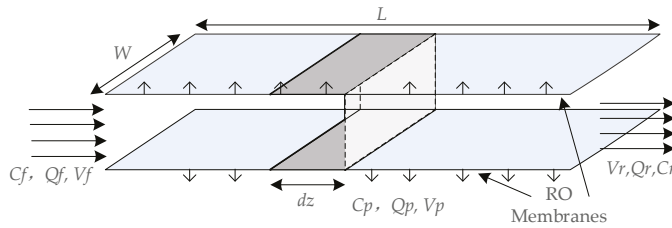


Figure 3. Schematic diagram of the inside of the feeding channel of the spiral wound RO modules.

3.1. RO Process Transport Model

Material conservation of solution:

$$Q_{p1} = Q_f - Q_{r1} \quad (1)$$

Material conservation of solute:

$$Q_f C_f = Q_{p1} C_{p1} + Q_{r1} C_{r1} \quad (2)$$

where Q_f and C_f are the flowrate and concentration of the feed water, respectively. Q_{p1} and C_{p1} are the flowrate and concentration of the water production side of the first-stage RO module, respectively. Q_{r1} and C_{r1} are the flowrate and concentration of the concentrated brine of the first-stage RO module, respectively.

The relationship between permeate flowrate and membrane parameters can be described using the following equation:

$$Q_{p1} = n_l w \int_0^L J_{v1} dz = W \int_0^L J_{v1} dz \quad (3)$$

Solvent flux:

$$J_{v1}(z) = A_w (\Delta P_{b1}(z) - \Delta \pi_{1(z)}) \quad (4)$$

Solute flux:

$$J_{s1}(z) = B_s (C_{m1}(z) - C_{p1}(z)) \quad (5)$$

Transmembrane pressure:

$$\Delta P_{b1}(z) = P_{b1}(z) - P_{p1}(z) \quad (6)$$

Osmotic pressure difference:

$$\Delta \pi_{1(z)} = RT (C_{m1}(z) - C_{p1}(z)) \quad (7)$$

Concentration polarization:

$$\phi_{1(z)} = \frac{C_{m1}(z) - C_{p1}(z)}{C_{b1}(z) - C_{p1}(z)} = \exp\left(\frac{J_{v1}(z)}{k_{c1}(z)}\right) \quad (8)$$

where n_l , w , L , and W are the number of leaves, width, effective length of the RO module, and the total width of the RO module, respectively. A_w and B_s refer to the transport parameters of the RO membrane for solvent and solute, respectively. $P_{b1}(z)$ and $P_{p1}(z)$ are the

brine pressure and produced water pressure at the z position of the first-stage RO module, respectively. $C_{m1(z)}$ and $C_{p1(z)}$ denote the brine concentration on the membrane surface at the z position of the first-stage RO module and the permeate water concentration on the permeate side, respectively. R and T are the gas constant and temperature, respectively. $\phi_{1(z)}$ is the concentration polarization phenomenon coefficient at the z position of the first-stage RO module. $C_{b1(z)}$ is the brine concentration at the z position of the first-stage RO module. $k_{c1(z)}$ is the mass transfer coefficient at the z position of the first-stage RO module.

The above equations are integrated as follows:

$$J_{v1(z)} = A_w((\Delta P_{b1(z)} - P_{p1(z)}) - RT(C_{m1(z)} - C_{p1(z)})) \quad (9)$$

$$J_{s1(z)} = B_s \exp\left(\frac{J_{v1(z)}}{k_{c1(z)}}\right)(C_{b1(z)} - C_{p1(z)}) \quad (10)$$

$$J_{s1(z)} = J_{v1(z)} C_{p1(z)} \quad (11)$$

The formula for calculating the mass transfer coefficient $k_{c1(z)}$ of concentration polarization is as follows:

$$Sh = \frac{k_{c1(z)} d_e}{D_{AB1(z)}} = k_1 Re^{0.875} Sc^{0.25} \quad (12)$$

Reynolds coefficient:

$$Re = \frac{\rho_{1(z)} V_{b1(z)} d_e}{\mu_{1(z)}} \quad (13)$$

Schmidt coefficient:

$$Sc = \mu_{1(z)} / (\rho_{1(z)} D_{AB1(z)}) \quad (14)$$

Here, $D_{AB1(z)}$ is the dynamic viscosity. Re and Sc denote the Reynolds coefficient and the Schmidt coefficient, and d_e is the equivalent diameter. k_1 is the coefficient. $\rho_{1(z)}$ is the brine density at the z position of the first-stage RO module. $V_{b1(z)}$ is the superficial feed velocity at the z position of the first-stage RO module. $\mu_{1(z)}$ is the dynamic viscosity of the solution at the z position of the first-stage RO module. The specific formulas of the above parameters are as follows:

Dynamic viscosity:

$$D_{AB1(z)} = \gamma_1 \cdot \exp(\gamma_2 C_{b1(z)} - \frac{2513}{273.15 + T}) \quad (15)$$

The density of brine in the channel:

$$\rho_{1(z)} = a_1 M + \sqrt{a_2 M^2 + a_3 M C_{b1(z)}} \quad (16)$$

The dynamic viscosity of brine in the channel:

$$\mu_{1(z)} = \alpha \cdot \exp(\beta C_{b1(z)} - \frac{1965}{273.15 + T}) \quad (17)$$

Variable M :

$$M = k - b \cdot T \quad (18)$$

Here, γ_1 and γ_2 are the coefficients in the dynamic viscosity formula, which are related to the temperature and composition of the solution, etc. a_1 , a_2 , a_3 , α , and β are the coefficients in the regression equation of coal-fired power plant wastewater treatment, and the variable M is inversely proportional to the temperature T .

The relationship between the local parameters of the RO module is as follows:

Local solution mass conservation:

$$Q_{b1(0)} = Q_{b1(z)} + Q_{p1(z)} \quad (19)$$

Local solute material conservation:

$$Q_{b1(0)}C_{b1(0)} = Q_{b1(z)}C_{b1(z)} + Q_{p1(z)}C_{p1(z)} \quad (20)$$

where $Q_{b1(0)}$, $Q_{b1(z)}$, and $Q_{p1(z)}$ refer to the feed water flowrate in the first-stage RO module, the brine water flowrate at the z position of the RO module, and the flowrate of the permeate water side, respectively. $C_{b1(0)}$, $C_{b1(z)}$, and $C_{p1(z)}$ represent the first-stage feed water concentration, the brine concentration at the z position of RO module, and the permeate water side concentration, respectively.

Local flowrate:

$$\frac{dQ_{b1(z)}}{dz} = -\frac{dQ_{p1(z)}}{dz} = -WJ_{v1(z)} \quad (21)$$

Pressure drop:

$$P_{d1(z)} = \frac{1}{2}\rho_{1(z)}\int_0^z \lambda \frac{V_{b1(z)}^2}{d_e} dz \quad (22)$$

$$\lambda = K_\lambda Re^{-0.3} \quad (23)$$

Local velocity:

$$V_{b1(z)} = V_{b1(0)} - \frac{2}{\varepsilon_{sp}} \int_0^L \frac{J_{v1(z)}}{H} dz \quad (24)$$

Local salt concentration:

$$C_{b1(z)} = \frac{V_{b1(0)}}{V_{b1(z)}}C_{b1(0)} - \frac{2C_{p1(z)}}{\varepsilon_{sp}V_{b1(z)}} \int_0^L \frac{J_{v1(z)}}{H} dz \quad (25)$$

Among them, $P_{d1(z)}$ is the pressure drop at the z position of the first RO module, k_λ represents the empirical value, $V_{b1(0)}$ is the feed water flowrate in the first stage, ε_{sp} is the membrane porosity, and H represents the height of the feed channel.

3.2. System Performance Model Equations

In the process of the RO modules shown in Figure 2, the RO modules of the two stages are of the same type, so the structure and principle of the membrane elements of the two stages are the same, and the above-mentioned transport model is also applicable to the second stage. The system model only needs to express the relationship between the feed water parameters of the second stage and the brine outlet of the first stage and the system performance relationship.

The parameters of the second stage of feed water flowrate are expressed as follows:

The second-stage feed water flowrate:

$$Q_{f2} = \frac{Q_{r1} \cdot NP1}{NP2} \quad (26)$$

The second-stage feed water concentration:

$$C_{f2} = C_{r1} \quad (27)$$

The second-stage feed water pressure:

$$P_{f2} = P_{r1} + P_{boost} \quad (28)$$

where $NP1$ and $NP2$ denote the number of pressure vessels in the first stage and the second stage of the RO system, respectively. P_{r1} , C_{r1} , and Q_{r1} are the pressure, concentration and flowrate of the first stage of brine treatment, respectively. P_{f2} , C_{f2} , and Q_{f2} refer to

the pressure, concentration, and flowrate of the second-stage feed water, respectively. P_{boost} represents the pressure of the booster pump.

Combining the above equations, the key performance parameters of the RO system equations are as follows:

Water recovery rate:

$$R_{ec} = \frac{Q_{p1} + Q_{p2}}{Q_f} \times 100\% \quad (29)$$

Salt rejection rate:

$$R_y = \left(1 - \frac{Q_{p1} \cdot C_{p1(L)} + Q_{p2} \cdot C_{p2(L)}}{Q_f \cdot C_f}\right) \times 100\% \quad (30)$$

Specific energy consumption:

$$SEC = \frac{P_f Q_f / (\varepsilon_p \cdot \varepsilon_{VFD}) + P_{boost} \cdot Q_{f2} / \varepsilon_{bp}}{Q_p} \quad (31)$$

Here, Q_f , C_f , and P_f are the flowrate, concentration, and pressure of the feed water of the RO modules, respectively. Q_{p1} and Q_{p2} represent the outlet water flowrate of the first stage and the outlet water flowrate of the second stage, respectively. $C_{p1(L)}$ and $C_{p2(L)}$ are the final concentrations of the first- and second-stage waters, respectively. ε_p , ε_{VFD} , and ε_{bp} refer to the mechanical efficiency of the high-pressure pump, the mechanical efficiency of the variable frequency drive, and the mechanical efficiency of the booster pump, respectively.

4. Model Calibration and Simulation Analysis

4.1. Model Parameter Calibration

Since the parameters of the seawater desalination model do not fit in the coal-fired power plant wastewater treatment model, the model is calibrated with the smallest variance between the model calculated data and the data output by the design software as the objective function. The optimization is solved by solvers, such as IPOPT and CONOPT of the GAMS platform [20]. Its specific optimization proposition is as follows:

Objective function:

$$\min_{A_w, B_s, K_\lambda, k_1, \gamma_1, \gamma_2} E(\theta) = \min_{A_w, B_s, K_\lambda, k_1, \gamma_1, \gamma_2} \sum_{i=0}^n \omega_i (y_{icalc} - y_{imeas})^2$$

Such that:

$$\begin{aligned} f(x, u, v) &= 0 \\ A_w^L &\leq A_w \leq A_w^U \\ B_s^L &\leq B_s \leq B_s^U \\ K_\lambda^L &\leq K_\lambda \leq K_\lambda^U \\ k_1^L &\leq k_1 \leq k_1^U \\ \gamma_1^L &\leq \gamma_1 \leq \gamma_1^U \\ \gamma_2^L &\leq \gamma_2 \leq \gamma_2^U \end{aligned}$$

where y_{icalc} represents the calculated value of the model, y_{imeas} represents the output value of the design software, ω_i represents the weight, the superscripts L and U refer to the lower and upper bounds of the parameter, and the $f(x, u, v) = 0$ equation represents the RO process model of the system.

Through the optimization and solution of the above proposition, we can obtain the optimal model parameters and finally the correct mechanistic model for coal-fired power plant wastewater treatment.

In order to better study the modeling and optimization process of the system, this paper takes a coal-fired power plant wastewater resource utilization system in Inner

Mongolia as an example. In the process flow chart shown in Figure 2, the RO device of this system is a two-stage membrane module. The RO modules of this system use the PROC10 from Hydranautics. The PROC10 membrane module is an enhanced, low-polluting, low-pressure RO composite membrane, which has the advantages of high salt rejection, a low pressure drop, less fouling, easy cleaning, and a long life. The parameters of the membrane module are shown in Table 1. The water quality parameters of the coal-fired power plant wastewater at the feed port of the RO system are shown in Table 2.

Table 1. Membrane element property.

Membrane Property	Unit	Value
RO membrane model	—	PROC10
Membrane material	—	Aromatic polyamide composites
Maximum flowrate	m ³ /h	240
Maximum pressure	bar	41.4
Maximum temperature	°C	45
Maximum SDI	—	5
Effective area	m ²	479.7
Effective membrane leaf length	m	0.91
Effective membrane leaf width	m	0.704
Inlet mesh thickness	mm	0.8636
Pump efficiency	—	0.75

Table 2. Water quality parameters of coal-fired power plant wastewater.

Property	Result (mg/L)	Property	Result
K ⁺	89.00	Total alkalinity	16.4 mmol/L
Na ⁺	4030.00	Alkalinity, PPM CaCO ₃	16.2 mmol/L
1/2Ca ²⁺	268.54	Total silica	26.3 mg/L
1/2Mg ²⁺	36.45	Inactive silicon	7.1 mg/L
NH ₄ ⁺	8.12	TDS	13,668.0 mg/L
1/2Sr ²⁺	8.80	SS	8.0 mg/L
1/2Ba ²⁺	0.11	Ammonia nitrogen	6.30 mg/L
1/3Fe ³⁺	0.29	TUB	0.396 NTU
Cl [−]	2480.00	CODCr	51.0 mg/L
1/2SO ₄ ^{2−}	5201.00	PH (25 °C)	8.27
HCO ₃ [−]	964.12	Water temperature	15 °C
1/2CO ₃ ^{2−}	12.00	Water pressure	20.8 bar
NO ₃ [−]	445.9	Water flowrate	88.0 m ³ /h
F [−]	6.90	Water concentration	13,600.0 mg/L

We established and calibrated the RO system model, as the model of Hydranautics' design software IMSDesign is confidential, and the software is calculated off-line and cannot simulate the RO system in real time. When the plant was designed, it was simulated in advance through the IMSDesign software. Hence, the GAMS calculation data were first compared with the output data of the IMSDesign software, and the correctness of the model was verified based on this. The above data were used as the input of the GAMS platform and the IMSDesign software, respectively, and the results of the model calculation were outputted. In view of the different calculation methods of the model, only the final operating results of the RO system were compared, and the intermediate results of the RO system were no longer compared. The comparison results are shown in Table 3.

Table 3. Data comparison.

Data Sources	Concentration of the First-Stage Permeate (m ³ /h)	Concentration of the Second-Stage Permeate (m ³ /h)	Final Product Water Concentration (m ³ /h)	Second-Stage Inlet Pressure (Bar)
Model data before correction	0.155	0.140	0.148	31.0
Corrected model data	0.228	0.489	0.308	32.1
IMSDesign's data	0.192	0.495	0.289	31.4

From the comparison of the model data before and after correction in Table 3, it can be seen that the calibrated parameters of the model improved the accuracy of the model. By comparing the calculated data of the calibrated model with the data of the design software IMSDesign, the maximum difference between the permeate concentration of each section and the final permeate concentration was 0.036 m³/h; the errors of the first and second stage were 15.7% and 1.2%, respectively; and the error of the feed water pressure was 2.2%. Only the first stage had a large error with respect to the concentration of the produced water; the rest of the errors were relatively small. In the actual operation of the power plant, these errors are acceptable, and the validity of the model is proved for the first time.

To further verify the correctness of the model, the actual data for the plant were compared with the output data of GAMS. Read the plant RO module feed water flowrate, the feed water pressure, and the feed pump outlet concentration as inputs to the GAMS simulation program. The feed concentration is converted by the read conductance value as shown in Equation (32).

$$C_f = K * EC_{25^{\circ}C} / 1000 \quad (32)$$

K represents the conversion coefficient, which is related to the impurity content in the solution, and the value here is 0.67. $EC_{25^{\circ}C}$ represents the conductivity value converted to the reference temperature of 25 °C.

Three groups of available data are selected for calculation and comparison, among which the readable data of the power plant and the output data of GAMS are shown in Table 4. The feed water flowrate of the RO modules, the feed water pressure of the first stage of the RO modules, and the outlet concentration of the feed pump are used as the feeding conditions for GAMS simulation. From the table data, the errors of the RO module permeate water flowrate are 6.26%, 5.77%, and 1.32%, respectively. The errors of the feed water flowrate of the RO module booster pump are 7.59%, 2.41% and 16.43%, respectively. The errors of RO module concentrated water flowrate are 12.97%, 5.57%, and 2.50%, respectively. The permeate water pressure errors of the first stage of the RO modules are 0.05%, 4.53%, and 1.21%, respectively. The errors of the concentrated water pressure of the RO modules are 2.10%, 2.65%, and 2.10%, respectively. The reason for the errors between the power plant data and the GAMS output data may be the drift of the sensor, so the above comparison data once again clarify the correctness of the model.

Table 4. Comparison of power plant data and simulation data.

Properties	Data 1		Data 2		Data 3	
	Power Plant Data	GAMS Data	Power Plant Data	GAMS Data	Power Plant Data	GAMS Data
Feed water flowrate of RO modules (m ³ /h)	64.4383	64.4383	72.7411	72.7411	79.7619	79.7619
Feed water pressure of the first stage (bar)	22.75	22.75	22.7885	22.7885	21.7115	21.7115
Feed pump outlet conductivity EC _{25°C} (μS/cm)	19,887.1	19,887.1	17,994.5	17,994.5	16,712.5	16,712.5
Water production flowrate of the first stage (m ³ /h)	—	34.9644	—	41.4348	—	45.0576
Water production flowrate of the second stage (m ³ /h)	—	7.1106	—	8.1844	—	9.8966
RO module water production flowrate (m ³ /h)	44.8824	42.0750	52.6563	49.6192	55.6918	54.9542
Feed water flowrate of RO modules booster pump (m ³ /h)	27.3962	29.4744	30.5708	31.3068	41.5293	34.7040
Concentrate water flowrate of RO modules (m ³ /h)	19.7955	22.3636	21.9017	23.1224	25.4426	24.8073
Water production pressure in the first stage (bar)	22.2885	22.2993	23.2885	22.2517	21.3269	21.0693
Concentrated water pressure of RO modules (bar)	28.4423	29.0406	29.7500	28.9632	28.4423	29.0406
Salt rejection rate (%)	97.4835	98.6559	98.7274	98.7235	97.4835	98.6559

4.2. Model Simulation Analysis

After verifying the validity of the model, the system performance changes corresponding to different parameters were simulated and calculated. Through the simulation, the internal states of the RO system can be displayed intuitively, so that those unmeasurable states can be displayed. Figures 4–7 show the calculated results of the parameters given in Tables 1 and 2 for the two-stage RO system. From the process flow chart shown in Figure 2, it can be noted that there is a booster pump between the first stage and the second stage. This booster pump of the RO system enables the feed flowrate, permeate flux, concentration polarization, and other pressure-related parameters to jump in the second stage. In order to fully demonstrate the performance changes of the RO system, all the following research results show the calculation data for the first and second stages are shown in same figure.

It can be seen from the simulation results that the feed flowrate, permeate flux, and concentration polarization of the two-stage membrane modules all show an approximate linear decreasing trend. The main reason is that when the feed water is treated into fresh water and concentrated brine, as the osmotic pressure of the RO modules increases, the driving force remains unchanged and the feed flowrate, permeate flux, and concentration polarization decrease. Since the brine concentration has little correlation with the increase in feed water pressure, Figure 7 shows that the brine concentration in the membrane channel continues to increase along the membrane channel.

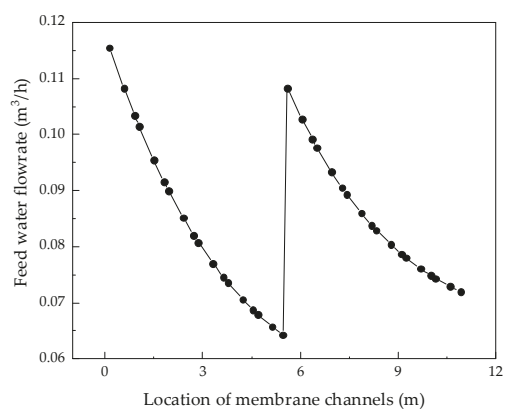


Figure 4. Variation curve of feed flow rate along the membrane channel.

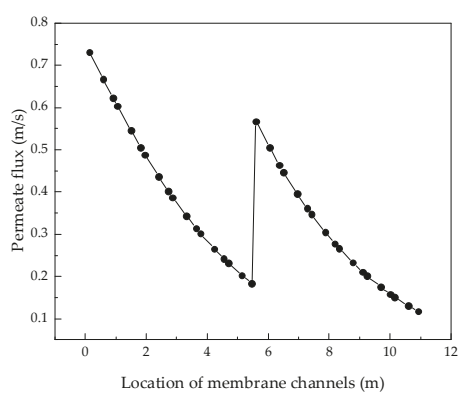


Figure 5. Variation curve of permeate flux along the membrane channel.

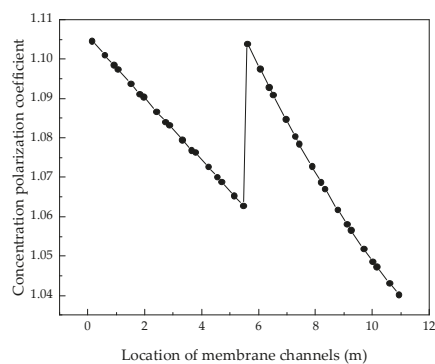


Figure 6. Variation curve of concentration polarization along the membrane channel.

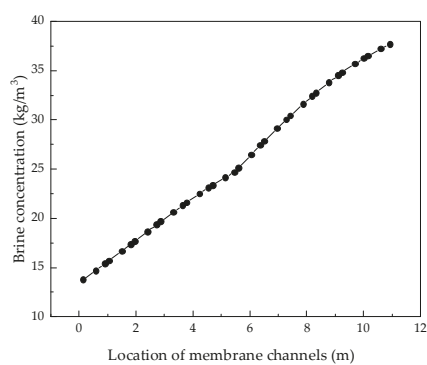


Figure 7. Variation curve of brine concentration along the membrane channel.

The above analysis has obtained the internal operation of the system. In order to understand the characteristics of the system more comprehensively, the following analyzes the influence of the coal-fired power plant wastewater flowrate, temperature, pressure, and concentration at the inlet of the RO modules on the system performance. In the analytic process, other parameters are fixed and only the analyzed variable parameter is changed; then, the simulation calculation is carried out so as to observe the different effects of different parameters of the coal-fired power plant wastewater at the entrance of the RO modules on the system's performance.

4.2.1. Effect of Feed Water Flowrate on System Performance

During the operation of the coal-fired power plants, the feed water flowrate of the RO modules is unstable because the RO modules are not always in operation. It can be seen from Table 1 that the maximum flowrate of the membrane module is $240.0 \text{ m}^3/\text{h}$, so, keeping other parameters unchanged, the influence of the membrane modules' feed water flowrate, from $60.0 \text{ m}^3/\text{h}$ to $216.0 \text{ m}^3/\text{h}$, on system performance can be analyzed. The analysis results for permeate flux, water production, water recovery rate, salt rejection rate, and specific energy consumption are shown in Figures 8–11.

Analysis of the above results show that with the increase in the feed water flowrate of the RO modules, the permeate flux increases, which leads to an increase in water production, but if the feed water flowrate is too high, the water production becomes stable or even decreases. The reason for the above phenomenon is that the velocity in the feed channel is positively related to the feed water flowrate so that when the feed water flowrate increases, the flowrate on the membrane surface increases correspondingly. When the flowrate is less than $180 \text{ m}^3/\text{h}$, the wastewater in the pipeline has enough time to penetrate, so water production increases with the increase in the flowrate. However, when the feed water flowrate is greater than $180 \text{ m}^3/\text{h}$, the water does not have enough time to penetrate, resulting in a decrease in water production.

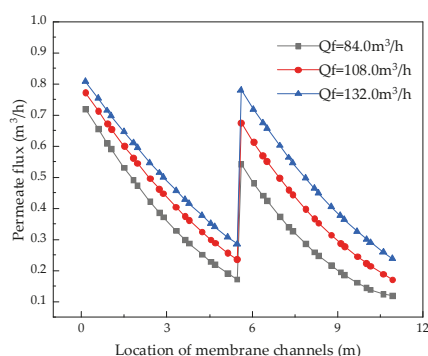


Figure 8. Effect of changes in feed water flowrate on permeate flux.

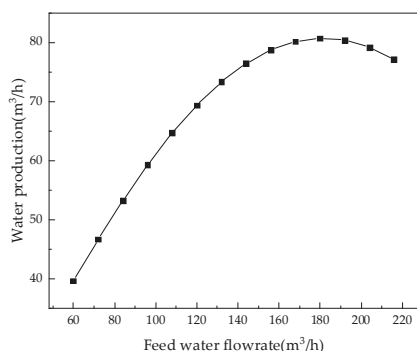


Figure 9. Effect of changes in feed water flowrate on water production.

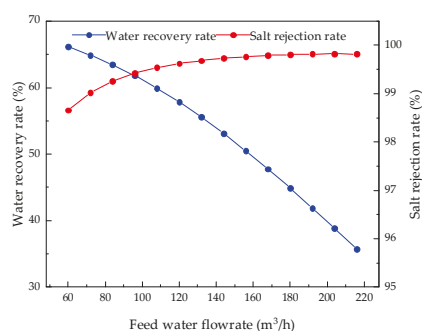


Figure 10. Effects of changes in feed water flowrate on water recovery rate and salt rejection rate.

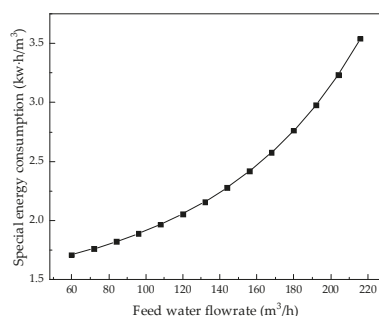


Figure 11. Effects of changes in feed water flowrate on the specific energy consumption.

Figures 10 and 11 analyze the effect of feed water flowrate on system performance parameters. Figure 11 shows that with an increase in the feed water flowrate, the water recovery rate of the system decreases, while the salt rejection rate increases and the growth rate of the salt rejection rate continues to slow down. Similarly, with the continuous increase in flowrate, the residence time of the feed wastewater in the pipeline is greatly shortened. In this case, neither water nor salt has enough time to pass to the permeate side, so the water recovery rate decreases. As the feed water flowrate increases, the velocity at the membrane surface increases, so the pressure rises, reducing the concentration polarization, and thereby the salt rejection rate is slightly increased. Figure 11 shows that as the feed water flowrate increases, the specific energy consumption also increases. With an increase in the feed water flowrate, the velocity at the membrane surface increases, the pressure in the pipeline rises, and more energy consumption is needed to produce water per unit volume.

4.2.2. Effect of Feed Temperature on System Performance

The RO membrane is very sensitive to changes in the feed water temperature. Therefore, we kept other parameters unchanged and analyzed the influence of feed temperature from 5 °C to 25 °C on system performance. Figures 12–15 illustrate the effects of feed water temperature on RO system performance.

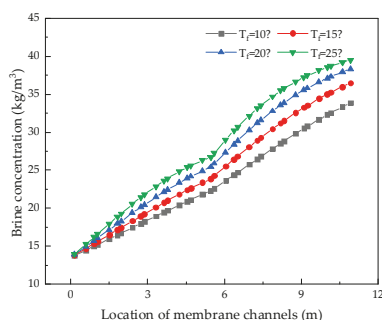


Figure 12. Effect of changes in feed water temperature on brine concentration.

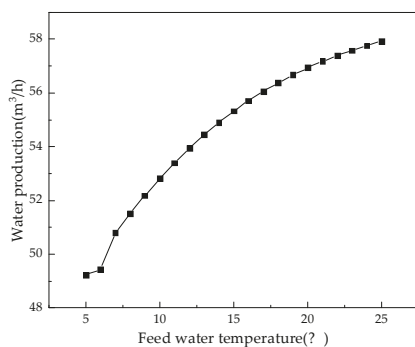


Figure 13. Effect of changes in feed water temperature on water production.

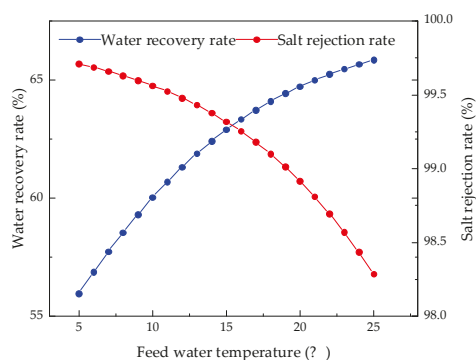


Figure 14. Effects of feed water temperature changes on water recovery rate and salt rejection rate.

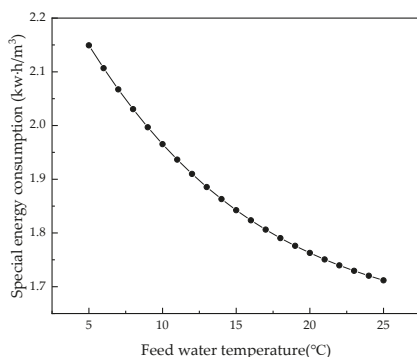


Figure 15. Effect of changes in feed water temperature on specific energy consumption.

It can be seen from Figures 12 and 13 that as the feed water temperature increases, the brine concentration in the membrane channel increases accordingly. The water production of the RO modules also increases, and the water production increases (or decreases) by 0.3% to 2.5% for every 1 °C increase (or decrease) in the feed water temperature. Since, with an increase in the feed water temperature, the viscosity of water molecules decreases and the diffusivity increases, and with an increase in the moving speed, the water production increases, the brine concentration in the membrane channel also increases. Figures 14 and 15 illustrate the effects of temperature on system performance. As the temperature increases, the water recovery rate of the system increases, while the salt rejection rate and specific energy consumption decrease. An increase in the feed water temperature also accelerates the movement of molecules so that the membrane modules pass through more water and salt, and as the water recovery rate of the system increases, so the concentration of brine in the pipeline will increase. An increase in permeated salt is accompanied by a decrease in the salt rejection rate. The higher the temperature, the faster the water molecules move and the less energy is required.

4.2.3. Effect of Feed Water Pressure on System Performance

Keeping other parameters unchanged, we analyzed the influence of feed water pressure from 12.0 bar to 30.0 bar on system performance. Figures 16–19 illustrate the effects of feed water pressure on RO system performance.

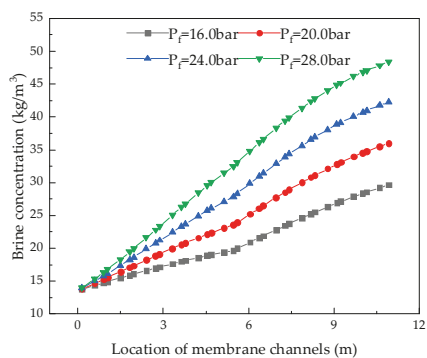


Figure 16. Effect of changes in feed pressure on brine concentration.

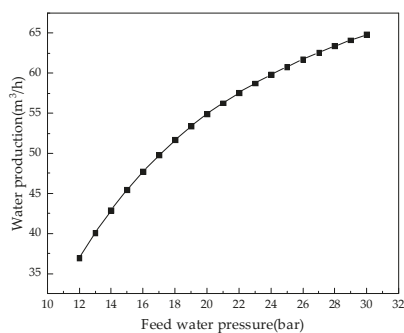


Figure 17. Effect of changes in feed water pressure on water production.

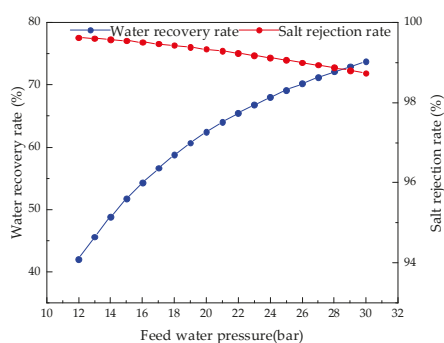


Figure 18. Effects of changes in feed water pressure on water recovery and salt rejection rate.

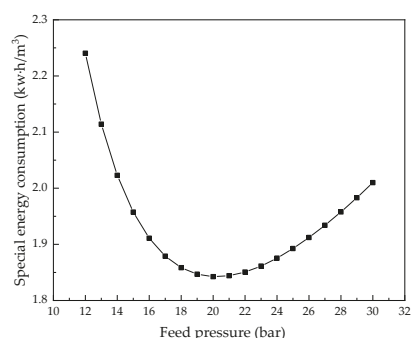


Figure 19. Effect of changes in feed water pressure on specific energy consumption.

From the analysis of the above figures, it can be seen that an increase in the feed water pressure increases the brine concentration in the membrane channel, water production, and the water recovery rate of the system. The increase in feed water pressure increases the driving force of the RO module, resulting in an increase in water production. The increased permeate water dilutes the salts permeating the membrane, resulting in a higher water recovery rate. With an increase in pressure, the excessively high salt rejection rate increases the concentration polarization, which leads to an increase in salt permeation, which offsets the increased water production, resulting in a slight decrease in the desalination rate. As the feed water pressure increases, the specific energy consumption first decreases and then increases, so there is a minimum value. As the net pressure driving the RO modules increases, the specific energy consumption required to generate a unit volume of permeate water decreases. When the feed water pressure exceeds a certain value, the concentration polarization is increased, which increases the specific energy consumption.

4.2.4. Effect of Feed Concentration on System Performance

Keeping other parameters unchanged, we analyzed the influence of feed concentration from 10.0 kg/m^3 to 27.0 kg/m^3 on the system. Figures 20–23 demonstrate the effect of feed pressure on RO system performance.

Figures 20 and 21 show that as the feed concentration increases, the osmotic pressure increases, while the driving force remains unchanged, resulting in a linear downward trend in water production and an increase in brine concentration in the membrane channel, which eventually converges. This is because, with the increase in the feed concentration, the osmotic pressure of the feed water becomes higher and the driving force decreases, thereby reducing water production.

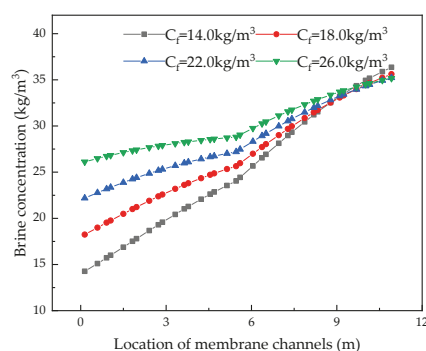


Figure 20. Effects of changes in feed concentration on brine concentration.

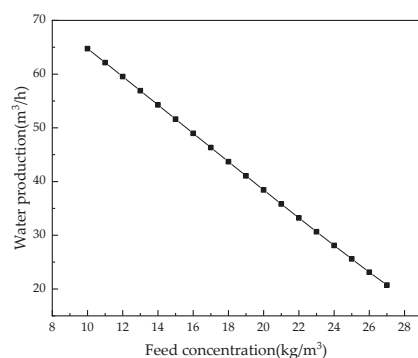


Figure 21. Effect of changes in feed concentration on water production.

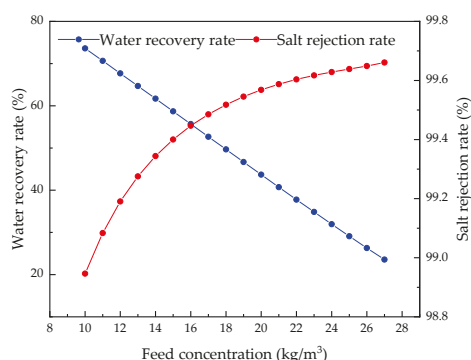


Figure 22. Effects of changes in feed concentration on water recovery and salt rejection rate.

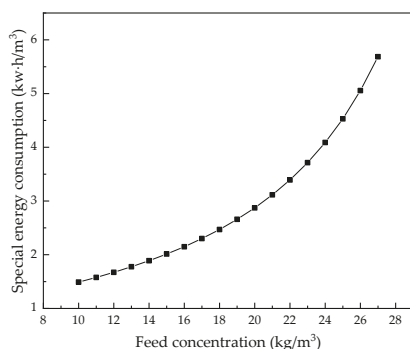


Figure 23. Effect of changes in feed concentration on specific energy consumption.

Figures 22 and 23 show that, as the feed concentration increases, water production decreases, resulting in a decrease in water recovery rate. With an increase in feed concentration, a small amount of salt is permeated, but due to the tight structure of the RO membrane and the rapid decline in water production, the permeated salt is offset so that the salt rejection rate of the system increases slightly. The increase in the osmotic pressure of the water supply and the decrease in the driving force require more energy consumption per unit volume of water, so the specific energy consumption increases.

5. Operational Optimization of the Membrane Treatment Process for Coal-Fired Power Plant Wastewater

Through the above simulation analysis, it is clear that the goal of the lowest specific energy consumption and daily average operating cost of the system can be achieved by adjusting the feed conditions of the system. Considering the actual operation of the coal-fired power plant wastewater treatment system, the variables for optimal operation are mainly the controllable factors of the RO system (the feed water pressure, the feed water flowrate, and the pressure of the booster pump), but uncontrollable factors (feed water temperature and feed water concentration) can also affect the performance of the system.

Therefore, in the operational optimization analysis for coal-fired power plant wastewater treatment, the feed temperature was selected as 15 °C and 25 °C, respectively, and the feed concentration was selected as 13.0 kg/m³ and 20.0 kg/m³, respectively. The optimization analysis of the lowest specific energy consumption and the lowest average daily operating cost under different working conditions was then carried out.

5.1. Operational Optimization Based on the Lowest Specific Energy Consumption

5.1.1. Establishment of the Optimization Proposition

The minimum specific energy consumption is the optimization goal, and its optimization proposition can be expressed as follows:

Objective function:

$$\text{Min}_{P_f, Q_f, P_{\text{boost}}} SEC$$

Constraints:

RO process model:

$$f(x, u, v) = 0$$

Device constraints:

$$\begin{aligned} P_f^L &\leq P_f \leq P_f^U \\ Q_f^L &\leq Q_f \leq Q_f^U \\ P_{\text{boost}}^L &\leq P_{\text{boost}} \leq P_{\text{boost}}^U \end{aligned}$$

Superficial feed velocity for RO modules:

$$V_f^L \leq V_f \leq V_f^U$$

Initial conditions:

$$\begin{aligned} P_b &= \begin{cases} P_f, z = 0 \\ P_r, z = L \end{cases} \\ C_b &= \begin{cases} C_f, z = 0 \\ C_r, z = L \end{cases} \end{aligned}$$

The superscripts L and U refer to the upper and lower limits of the parameters, and the $f(x, u, v) = 0$ equation represents the RO process model of the system. The upper and lower limits of the constraints are shown in Table 5.

Table 5. Operation limits.

Property	Value
Maximum feed water pressure (bar)	41.4
Maximum feed water flowrate (m ³ /h)	240
Minimum feed water flowrate (m ³ /h)	24
Maximum pressure of booster pump (bar)	30
Ø	1.5
Maximum superficial feed velocity (m/s)	0.38
Minimum superficial feed velocity (m/s)	0.038

5.1.2. Running Optimization Analysis

Based on the operational optimization proposition with the lowest specific energy consumption, solvers such as IPOPT and CONOPT are called through the GAMS platform to optimize the solution with the lowest specific energy consumption as the optimization goal. Under the setting parameters of the RO system for coal-fired power plant wastewater treatment, the following three cases are considered, which are solved through the GAMS platform, and the changes in system performance before and after optimization are compared:

Case 1: The fixed feed water temperature is 15 °C and the feed concentration is 13.6 kg/m³.

Case 2: The fixed feed water temperature is 25 °C and the feed concentration is 13.6 kg/m³.

Case 3: The fixed feed water temperature is 15 °C and the feed concentration is 20.0 kg/m³.

A comparative analysis before and after optimization is carried out for the above three situations. Before optimization, the fixed feed water pressure of the RO system for coal-fired power plant wastewater is 20.3 bar, the feed water flowrate is 88.0 m³/h, and the pressure of the booster pump is 12.0 bar. After optimization, considering the safety

and actual operation of the coal-fired power plant wastewater RO system, the upper and lower bounds of the operating pressure, the feed water flowrate, and the pressure of the booster pump are given in Table 5, and, based on the optimization proposition with the lowest specific energy consumption, the RO process is solved on the GAMS platform and the performance parameters of the system before and after optimization are compared.

Case 1 is optimized and solved; the optimal feeding conditions are obtained: the feed water pressure is 17.57 bar, the feed water flowrate is 72.1 m³/h, and the pressure of the booster pump is 14.12 bar. Table 6 presents the comparison results before and after Case 1 system optimization. Compared with the values before optimization, the water recovery rate of the optimized system increases by 11.2%, the salt rejection rate decreases by 0.8%, and the specific energy consumption decreases by 0.431 kw·h/m³, which is 23.6% lower than the original. The water recovery rate of the optimized system has been significantly improved, and the specific energy consumption has been significantly reduced, achieving the goal of reducing energy consumption. The salt rejection rate of the system has been reduced by 0.8%, which is within an acceptable range. However, the performance of the system is greatly improved.

Table 6. Performance comparison results before and after system optimization in Case 1.

System Performance Parameters	Before Optimization	Optimized
Water recovery rate (%)	63.3%	74.5%
Salt rejection rate (%)	99.3%	98.5%
Specific energy consumption (kw·h/m ³)	1.826	1.395

The temperature in Case 2 is 25 °C and the rest of the parameters remain unchanged. Case 2 is optimized and solved, and the optimal feeding conditions are obtained as follows: the feed water pressure is 21.28 bar, the feed water flowrate is 91.0 m³/h, and the pressure of the booster pump is 12.41 bar. Table 7 shows the comparison results before and after system optimization. Before and after system optimization, the water recovery rate of the system increases by 9.0%, the salt rejection rate decreases by 1.7%, and the specific energy consumption decreases by 0.319 kw·h/m³, which is 18.6% lower than the original. Overall, the performance of the optimized system is also greatly improved.

Table 7. Performance comparison results of the Case 2 system before and after optimization.

System Performance Parameters	Before Optimization	Optimized
Water recovery rate (%)	66.0%	75.0%
Salt rejection rate (%)	98.2%	96.5%
Specific energy consumption (kw·h/m ³)	1.715	1.396

The feed concentration in Case 3 is 20.0 kg/m³ and other parameters remain unchanged. Case 3 is optimized and solved, and the optimal feeding conditions are obtained as follows: the feed water pressure is 20.25 bar, the feed water flowrate is 57.1 m³/h, and the pressure of the booster pump is 11.52 bar. Table 8 shows the comparison results before and after system optimization. Before and after the system optimization, the water recovery rate of the system increases by 20.7%, the salt rejection rate decreases by 2.0%, and the specific energy consumption decreases by 1.19 kw·h/m³, which is 42.6% lower than the original. Although the salt rejection rate of the optimized system is reduced by 2.0%, the overall performance of the system is greatly improved.

Combining the above three optimized systems with different operating conditions, under the circumstance that the salt rejection rate of the optimized coal-fired power plant wastewater does not decrease by more than 2.0%, the water recovery rate and specific energy consumption of the system have been significantly improved. The purpose of reducing the energy consumption of the system has been achieved.

Table 8. Performance comparison results of Case 3 system before and after optimization.

System Performance Parameters	Before Optimization	Optimized
Water recovery rate (%)	44.2%	64.9%
Salt rejection rate (%)	99.6%	97.6%
Specific energy consumption (kw·h/m ³)	2.795	1.605

5.2. Operational Optimization Based on the Lowest Average Daily Operating Cost

5.2.1. Economic Model of Coal-Fired Power Plant Wastewater Treatment Operation Cost

To achieve the goal of the lowest average daily operating cost, firstly, it is indispensable to establish a correct economic model of the operating cost of coal-fired power plant wastewater treatment. Secondly, it is necessary to establish the correct optimization proposition. The optimization solution is carried out through the GAMS platform and the optimal strategy for the operational optimization of coal-fired power plant wastewater treatment can be obtained. The operating cost of the coal-fired power plant wastewater membrane treatment system can be divided into the following main component costs:

1. The operating costs of the feed water intake and pretreatment system mainly include: ① chemical addition cost (OC_{CH}), including acid, added scale inhibitors and flocculants, and other additives required to change hardness and composition; and ② water intake energy cost (OC_{IP}).
2. Operating electricity (energy) consumption (OC_{EN}), including the energy consumption of coal-fired power plant wastewater intake systems, high-pressure pumps, and booster pumps.
3. RO membrane replacement cost (OC_{ME}). According to the design and operating conditions, it is calculated at a replacement rate of about 15–20%.
4. Maintenance cost (OC_{MN}), including the maintenance costs for each element of the entire system, such as membrane, high pressure pump, booster pump, motor, etc.
5. Labor cost (OC_{LB}).

Among the above operating costs, the cost of chemical additives, water intake energy consumption, and operating energy consumption are related to the flowrate of the system, while the membrane replacement cost, maintenance cost, and labor cost are independent of flowrate. The specific operating costs corresponding to each part are as follows [34]:

Chemical additive cost:

$$OC_{CH} = kQ_f \quad (33)$$

where k is the conversion factor of chemical additive cost and Q_f represents the feed water flowrate of the RO system.

Water consumption cost:

$$OC_{IP} = \frac{P_o \cdot Q_f \cdot P_{elc}}{\eta_{IP}} \times PLF \quad (34)$$

Here, P_o refers to the outlet pressure of the intake pump, Q_f represents the feed water flowrate of the RO system, PLF is the load factor, P_{elc} denotes the electricity price, and η_{IP} is the efficiency of the coal-fired power plant wastewater intake pump.

Operating energy cost:

$$OC_{EN} = \left[\frac{P_f Q_f / (\varepsilon_p \cdot \varepsilon_{VFD}) + P_{boost} \cdot Q_{f2} / \varepsilon_{bp}}{Q_p} \right] \cdot P_{elc} \quad (35)$$

The operating energy cost mainly includes the energy consumption of the high-pressure pump and the booster pump. P_f represents the feed water pressure of the RO system. Q_{f2} and Q_p are the feed water flowrate of the second-stage RO module and the final water flowrate of the RO system, respectively.

RO membrane replacement cost:

$$OC_{ME} = Pri_{ME} \cdot NM \cdot \zeta_{re} / 360 \quad (36)$$

where Pri_{ME} denotes the unit price of RO membrane elements, NM is the total number of membrane elements of the RO system, and ζ_{re} represents the replacement rate of membrane modules.

When studying the average daily operating cost of the RO system for coal-fired power plant wastewater treatment, the RO cleaning and maintenance costs can be ignored, so the maintenance cost of the system can be expressed as the following equation:

Maintenance cost:

$$OC_{MN} = OC_{MNCON} = \omega OC_{RO} \quad (37)$$

Labor cost:

$$OC_{LB} = Pri_{LB} \cdot N_{LB} \quad (38)$$

$$N_{LB} = Q_p \cdot NP / 100 \quad (39)$$

ω is the proportion of maintenance costs, N_{LB} refers to the number of labor tasks, and Q_p represents the final water flowrate of the RO system.

Total operating cost:

$$\begin{aligned} OC &= OC_{IP} + OC_{EN} + OC_{MER} + OC_{MN} + OC_{CH} + OC_{LB} \\ &= OC_{IP} + OC_{EN} + OC_{MER} + OC_{MNCON} + OC_{CH} + OC_{LB} \\ &= OC_{IP} + OC_{EN} + OC_{MER} + 0.03 OC_{RO} + OC_{CH} + OC_{LB} \\ &= (OC_{IP} + OC_{EN} + OC_{MER} + OC_{CH} + OC_{LB}) / 0.97 \end{aligned} \quad (40)$$

5.2.2. Establishment of the Optimization Proposition

The lowest average daily operating cost of the coal-fired power plant wastewater RO system is the optimization goal, and its optimization proposition can be expressed as follows:

Objective function:

$$\underset{P_f, Q_f, P_{boost}}{\text{Min}} \quad OC$$

Constraints:

RO process model:

$$f(x, u, v) = 0$$

Operational cost model:

$$g(x, u, v) = 0$$

Device constraints:

$$\begin{aligned} P_f^L &\leq P_f \leq P_f^U \\ Q_f^L &\leq Q_f \leq Q_f^U \\ P_{boost}^L &\leq P_{boost} \leq P_{boost}^U \end{aligned}$$

Superficial feed velocity for RO modules:

$$V_f^L \leq V_f \leq V_f^U$$

Initial conditions:

$$\begin{aligned} P_b &= \begin{cases} P_f, z = 0 \\ P_r, z = L \end{cases} \\ C_b &= \begin{cases} C_f, z = 0 \\ C_r, z = L \end{cases} \end{aligned}$$

The superscripts L and U refer to the upper and lower limits of the parameters, the equation $f(x, u, v) = 0$ represents the RO process model of the system, and $g(x, u, v) = 0$ represents the operational cost model of the system.

5.2.3. Running Optimization Analysis

Based on the operational optimization proposition with the lowest average daily operating cost, solvers such as IPOPT and CONOPT are called through the GAMS platform to optimize the solution with the lowest average daily operating cost as the optimization goal. Under the setting parameters of the RO system for the coal-fired power plant wastewater treatment, the three operating conditions with the same optimization proposition with the lowest specific energy consumption are solved by the GAMS platform and the changes in the average daily operating costs of the system before and after optimization are compared:

Case 1: The fixed feed water temperature is 15 °C and the feed concentration is 13.6 kg/m³.

Case 2: The fixed feed water temperature is 25 °C and the feed concentration is 13.6 kg/m³.

Case 3: The fixed feed water temperature is 15 °C and the feed concentration is 20.0 kg/m³.

Before optimization, the fixed feed water pressure of the RO system for coal-fired power plant wastewater treatment is 20.3 bar, the feed water flowrate is 88.0 m³/h, and the pressure of the booster pump is 12.0 bar. After optimization, the upper and lower bounds of the feed water pressure, feed water flowrate, and booster pump pressure are given based on the consideration of the safety and actual operation of the coal-fired power plant wastewater RO system. Based on the optimization proposition with the lowest average daily operating cost, the RO process is solved on the GAMS platform and the performance parameters of the system before and after optimization are compared.

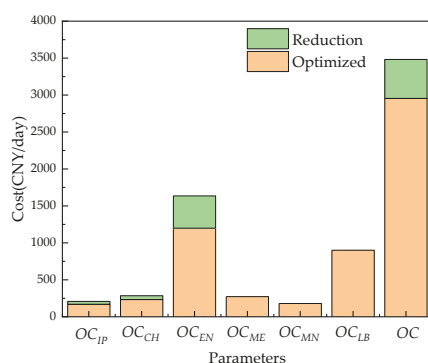
Among the system operating costs, labor costs, system maintenance costs, and membrane replacement costs have nothing to do with flowrate, so these values are fixed before and after optimization, but the proportions of these values change due to changes in other costs. Correspondingly, the energy consumption cost of pretreatment, chemical cost, and operating energy cost are related to the feed parameters of the system, so these values vary before and after optimization.

Table 9 and Figure 24 show the comparison results before and after system optimization. Under the operation of Case 1, the overall operating cost of the system before optimization is 3481.8 CNY/day, the cost of chemical agents accounts for 8.2%, the cost of operating energy accounts for 47.0%, and the cost of pretreatment energy accounts for 6.0%. After optimization, the overall operating cost of the system is 2954.9 CNY/day, which is 15.2% lower than that before optimization. The cost of chemical agents is reduced by 18.4%, the cost of operating energy consumption is reduced by 26.7%, and the cost of RO pretreatment energy consumption is reduced by 18.4%. It can be clearly seen that the operating cost of the RO system has been greatly reduced after the optimization of the RO system. The orange shading in Figure 24 represents the daily average operation cost of the RO system after optimization, the green represents the reduction in the daily average cost after optimization, and the total height represents the daily average operating cost before system optimization.

Table 10 and Figure 25 show the results before and after system optimization. Under the operation of Case 2, the overall operating cost of the system before optimization is 3447.3 CNY/day, the cost of chemical agents, the energy cost of the RO process, and the cost of operating energy consumption accounts for 8.3%, 52.4%, and 46.4%, respectively. After optimization, the total system operating cost is 2984.9 CNY/day, which is 13.4% lower than that before optimization. The cost of chemical agents is reduced by 15.0%, the operating energy consumption cost reduced by 15.0%, and there is an 18.4% reduction in pretreatment energy costs. It can be clearly seen that the operating cost of the RO system has been greatly reduced after the optimization of the RO system.

Table 9. Operational composition before and after RO system optimization.

Related Parameters	Before Optimization		After Optimization	
	Value (CNY/Day)	Proportion (%)	Value (CNY/Day)	Proportion (%)
Water intake energy cost (OC_{IP})	208.0	6.0	169.8	5.7
Chemical cost (OC_{CH})	285.0	8.2	232.6	7.9
Running energy cost (OC_{EN})	1635.7	47.0	1199.4	40.6
RO membrane replacement cost (OC_{ME})	273.1	7.9	273.1	9.2
Maintenance cost (OC_{MN})	180.0	5.1	180.0	6.1
Labor costs (OC_{LB})	900.0	25.8	900.0	30.5
Total cost of RO system (OC)	3481.8	100.0	2954.9	100.0

**Figure 24.** Comparison of the average daily operating costs of the system before and after optimization.**Table 10.** Operational composition before and after RO system optimization.

Related Parameters	Before Optimization		After Optimization	
	Value (CNY/Day)	Proportion (%)	Value (CNY/Day)	Proportion (%)
Water intake energy cost (OC_{IP})	208.0	6.0	176.7	5.9
Chemical cost (OC_{CH})	285.0	8.3	242.2	8.1
Running energy cost (OC_{EN})	1601.2	46.4	1212.9	40.6
RO membrane replacement cost (OC_{ME})	273.1	8.0	273.1	9.2
Maintenance costs (OC_{MN})	180.0	5.2	180.0	6.0
Labor costs (OC_{LB})	900.0	26.1	900.0	30.2
Total cost of RO system (OC)	3447.3	100.0	2984.9	100.0

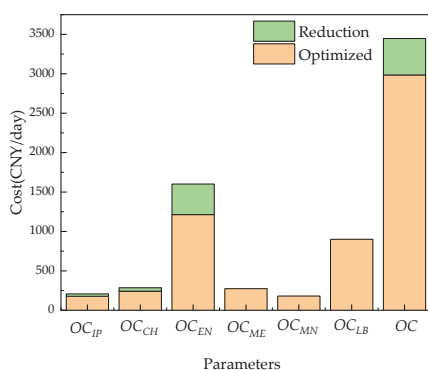
**Figure 25.** Comparison of the average daily operating costs of the system before and after optimization.

Table 11 and Figure 26 show the results before and after system optimization. Under the operation of Case 3, the overall operating cost of the system before optimization is

3593.7 CNY/day, the cost of chemical agents accounts for 7.9%, the cost of operating energy accounts for 48.6%, the cost of pretreatment energy consumption accounts for 5.8%. After optimization, the overall operating cost of the system is 2682.6 CNY/day, which is 25.4% lower than that before optimization. The cost of chemical agents is reduced by 36.3%, the cost of operating energy consumption is reduced by 41.9%, and the cost of RO pretreatment energy consumption is reduced by 36.3%. It can be clearly seen that the operating cost of the RO system has been greatly reduced after the optimization of the RO system.

Table 11. Operational composition before and after RO system optimization.

Related Parameters	Before Optimization		After Optimization	
	Value (CNY/Day)	Proportion (%)	Value (CNY/Day)	Proportion (%)
Water intake energy cost (OC_{IP})	208.0	5.8	132.6	4.9
Chemical cost (OC_{CH})	285.0	7.9	181.6	6.8
Running energy cost (OC_{EN})	1747.6	48.6	1015.3	37.9
RO membrane replacement cost (OC_{ME})	273.1	7.6	273.1	10.2
Maintenance costs (OC_{MN})	180.0	5.0	180.0	6.7
Labor costs (OC_{LB})	900.0	25.1	900.0	33.5
Total cost of RO system (OC)	3593.7	100.0	2682.6	100.0

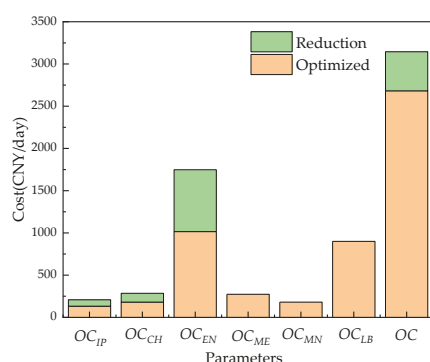


Figure 26. Comparison of the average daily operating costs of the system before and after optimization.

In summary, the increase in feed temperature reduces the average daily operating energy consumption of the system and the increase in feed concentration increases the daily average operating energy consumption of the system. For the operational optimization analysis under the above three different operating conditions, after the optimization, the daily average total operating cost of the system has decreased significantly, reaching the goal of reducing the average daily operating cost.

6. Conclusions

RO technology is important not only for seawater desalination but also for coal-fired power plant wastewater treatment. In this paper, a coal-fired power plant system in Inner Mongolia was taken as an example to study the simulation and optimization of the membrane treatment process of coal-fired power plant wastewater. Firstly, based on the solution–diffusion theory, pressure drop, and osmotic concentration polarization phenomena, a mechanistic model equation of the RO process of coal-fired power plant wastewater treatment was completed by drawing on the seawater desalination process. Through the correction of model parameters, a system model suitable for coal-fired power plant wastewater treatment was obtained. Secondly, in view of the opaqueness of the resource treatment process, a simulation analysis of the coal-fired power plant wastewater treatment process was carried out and internal data for the coal-fired power plant wastewater RO treatment process were obtained, realizing the transparent management of the system.

Finally, an optimization analysis of the coal-fired power plant wastewater treatment system was carried out.

Focusing on the problem of high energy consumption in the resource treatment of coal-fired power plant wastewater by the RO process, an optimization and analysis of a coal-fired power plant wastewater RO treatment system was carried out. To begin with, an optimization analysis of three different working conditions was performed, with the lowest specific energy consumption as the optimization goal. The water recovery rate was increased by 11.2%, 9.0%, and 20.7%, and the specific energy consumption was decreased by 23.6%, 18.6%, and 42.6%, respectively, which fully proved the effectiveness of the optimization strategy. Afterwards, taking the lowest average daily operating cost as the optimization goal, the same three working conditions were analyzed. The average daily operating costs of the system were reduced by 526.9 CNY/day, 462.4 CNY/day, and 911.1 CNY/day, which also proved the effectiveness of the optimization strategy. Therefore, the simulation and optimization research on the recycling process of coal-fired power plant wastewater presented here can promote the treatment of coal-fired power plant wastewater and is significant for the development of zero-emission coal-fired power plant wastewater treatment systems.

Author Contributions: Conceptualization, L.H.; methodology, Y.X. and A.J.; validation, L.H. and C.L.; investigation, Y.Z. and F.X.; writing—original draft preparation, L.H. and Y.X.; writing—review and editing, A.J. and C.L.; supervision, Y.Z. and F.X. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Zhejiang Provincial Natural Science Foundation, grant number LY20F030010, and the National Natural Science Foundation of China, grant number 61973102.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data is contained within the article.

Acknowledgments: The authors gratefully acknowledge CHN ENERGY LUCENCY Enviro-tech Co., LTD. for financial support.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Goh, P.S.; Ismail, A.F. A review on inorganic membranes for desalination and wastewater treatment. *Desalination* **2018**, *434*, 60–80. [CrossRef]
2. Blandin, G.; Verliefde, A.R.D.; Comas, J.; Rodriguez-Roda, I.; Le-Clech, P. Efficiently combining water reuse and desalination through forward osmosis—reverse osmosis (FO-RO) hybrids: A critical review. *Membranes* **2016**, *6*, 37. [CrossRef] [PubMed]
3. Lee, S.; Kim, Y.; Hong, S. Treatment of industrial wastewater produced by desulfurization process in a coal-fired power plant via FO-MD hybrid process. *Chemosphere* **2018**, *210*, 44–51. [CrossRef]
4. Zhu, F.; Wang, Y.; Xu, Z.; Li, J.; Dong, Y.; Li, H.; Li, X.; Hu, Y.; Sun, X.; Ding, L. Research on the development path of carbon peaking and carbon neutrality in China's power industry. *Power Technol. Environ. Prot.* **2021**, *37*, 1674–8069.
5. Redondo, J.A. Brackish-, sea- and wastewater desalination. *Desalination* **2001**, *138*, 29–40. [CrossRef]
6. Hanchang, S.H.I. Industrial wastewater-types, amounts and effects. *Point Sources Pollut. Local Eff. Control.* **2009**, *2*, 191–202.
7. Obotey Ezugbe, E.; Rathilal, S. Membrane technologies in wastewater treatment: A review. *Membranes* **2020**, *10*, 89. [CrossRef]
8. Sonune, A.; Ghate, R. Developments in wastewater treatment methods. *Desalination* **2004**, *167*, 55–63. [CrossRef]
9. Ali, A.; Nymann, M.C.; Christensen, M.L.; Quist-Jensen, C.A. Industrial Wastewater Treatment by Nanofiltration—A Case Study on the Anodizing Industry. *Membranes* **2020**, *10*, 85. [CrossRef]
10. Thiruvengkatachari, R.; Francis, M.; Cunningham, M.; Su, S. Application of integrated forward and reverse osmosis for coal mine wastewater desalination. *Sep. Purif. Technol.* **2016**, *163*, 181–188. [CrossRef]
11. Choi, B.G.; Zhan, M.; Shin, K.; Hong, S. Pilot-scale evaluation of FO-RO osmotic dilution process for treating wastewater from coal-fired power plant integrated with seawater desalination. *J. Membr. Sci.* **2017**, *540*, 78–87. [CrossRef]
12. Al-Obaidi, M.A.; Ruiz-García, A.; Hassan, G.; Li, J.P.; Kara-Zaitri, C.; Nuez, I.; Mujtaba, I.M. Model Based Simulation and Genetic Algorithm Based Optimization of Spiral Wound Membrane RO Process for Improved Dimethylphenol Rejection from Wastewater. *Membranes* **2021**, *11*, 595. [CrossRef] [PubMed]

13. Malek, A.; Hawlader, M.N.A.; Ho, J.C. Design and economics of RO seawater desalination. *Desalination* **1996**, *105*, 245–261. [CrossRef]
14. Al-Bastaki, N.M.; Abbas, A. Modeling an industrial reverse osmosis unit. *Desalination* **1999**, *126*, 33–39. [CrossRef]
15. Karabelas, A.J.; Kostoglou, M.; Koutsou, C.P. Modeling of spiral wound membrane desalination modules and plants—review and research priorities. *Desalination* **2015**, *356*, 165–186. [CrossRef]
16. Al-Enezi, G.; Fawzi, N. Design consideration of RO units: Case studies. *Desalination* **2003**, *153*, 281–286. [CrossRef]
17. Oh, H.J.; Hwang, T.M.; Lee, S. A simplified simulation model of RO systems for seawater desalination. *Desalination* **2009**, *238*, 128–139. [CrossRef]
18. Kaghazchi, T.; Mehri, M.; Ravanchi, M.T.; Kargari, A. A mathematical modeling of two industrial seawater desalination plants in the Persian Gulf region. *Desalination* **2010**, *252*, 135–142. [CrossRef]
19. Lu, Y.; Hu, Y.; Xu, D.; Wu, L. Optimal design of reverse osmosis desalination system. *Water Treat. Technol.* **2005**, *3*, 9–14.
20. Marcovecchio, M.G.; Aguirre, P.A.; Scenna, N.J. Global optimal design of reverse osmosis networks for seawater desalination: Modeling and algorithm. *Desalination* **2005**, *184*, 259–271. [CrossRef]
21. Luo, H.; Jing, D.W. Operation Mathematical Model of Reverse Osmosis Membrane Element. *J. Tianjin Urban Constr. Inst.* **2006**, *1*, 47–49, 54.
22. Kim, D.Y.; Gu, B.; Yang, D.R. An explicit solution of the mathematical model for osmotic desalination process. *Korean J. Chem. Eng.* **2013**, *30*, 1691–1699. [CrossRef]
23. Gong, M.; Jiang, A.; Zhang, Q.; Wang, H.; Hu, J.; Lin, Y. An Improved Finite Element Meshing Strategy for Dynamic Optimization Problems. *Math. Probl. Eng.* **2017**, *2017*, 4829195. [CrossRef]
24. Blechschmidt, J.; Ernst, O.G. Three ways to solve partial differential equations with neural networks—A review. *GAMM-Mitt.* **2021**, *44*, e202100006. [CrossRef]
25. Cai, Q.; Lee, B.C.Y.; Ong, S.L.; Hu, J. Application of a Multiobjective Artificial Neural Network (ANN) in Industrial Reverse Osmosis Concentrate Treatment with a Fluidized Bed Fenton Process: Performance Prediction and Process Optimization. *ACS EST Water* **2021**, *1*, 847–858. [CrossRef]
26. Wang, L.; Cao, T.; Dykstra, J.E.; Proada, S.; Biesheuvel, P.M.; Elimelech, M. Salt and Water Transport in Reverse Osmosis Membranes: Beyond the Solution-Diffusion Model. *Environ. Sci. Technol.* **2021**, *55*, 16665–16675. [CrossRef] [PubMed]
27. Bonny, T.; Kashkash, M.; Ahmed, F. An efficient deep reinforcement machine learning-based control reverse osmosis system for water desalination. *Desalination* **2022**, *522*, 115443. [CrossRef]
28. Salgado-Reyna, A.; Soto-Regalado, E.; Gómez-González, R.; Cerino-Córdova, F.J.; García-Reyes, R.B.; Garza-González, M.T.; Alcalá-Rodríguez, M.M. Artificial neural networks for modeling the reverse osmosis unit in a wastewater pilot treatment plant. *Desalin. Water Treat.* **2015**, *53*, 1177–1187. [CrossRef]
29. Al-Obaidi, M.A.; Li, J.P.; Kara-Zaitri, C.; Mujtaba, I.M. Optimization of reverse osmosis based wastewater treatment system for the removal of chlorophenol using genetic algorithms. *Chem. Eng. J.* **2017**, *316*, 91–100. [CrossRef]
30. Fujioka, T.; Oshima, N.; Suzuki, R.; Price, W.E.; Nghiem, L.D. Probing the internal structure of reverse osmosis membranes by positron annihilation spectroscopy: Gaining more insight into the transport of water and small solutes. *J. Membr. Sci.* **2015**, *486*, 106–118. [CrossRef]
31. Song, L.; Hong, S.; Hu, J.Y.; Ong, S.L. Simulations of Full-Scale Reverse Osmosis Membrane Process. *J. Environ. Eng.* **2002**, *128*, 960–966. [CrossRef]
32. Damak, K.; Ayadi, A.; Zeghmami, B.; Schmitz, P. A new Navier-Stokes and Darcy's law combined model for fluid flow in crossflow filtration tubular membranes. *Desalination* **2004**, *161*, 67–77. [CrossRef]
33. Jiang, A.; Wang, H.; Lin, Y.; Cheng, W.; Wang, J. A study on optimal schedule of membrane cleaning and replacement for spiral-wound SWRO system. *Desalination* **2017**, *404*, 259–269. [CrossRef]
34. Lu, Y.; Hu, Y.; Xu, D.; Wu, L. Optimum design of reverse osmosis seawater desalination system considering membrane cleaning and replacing. *J. Membr. Sci.* **2006**, *282*, 7–13. [CrossRef]

Article

Modeling and Simulation of Either Co-Current or Countercurrent Operated Reverse-Osmosis-Based Air Water Generator

Marc Fill and Mirko Kleingries *

Institute of Mechanical Engineering and Energy Technology, Lucerne University of Applied Sciences and Arts, Technikumstrasse 21, CH-6048 Horw, Switzerland; marc.fill@hslu.ch

* Correspondence: mirko.kleingries@hslu.ch; Tel.: +41-41-349-32-86

Abstract: Technologies for obtaining drinkable water are becoming more important as global water consumption steadily increases and climate change progresses. One possibility for obtaining water is the extraction of water vapor from ambient air by means of air water generators (AWG). Previous studies in the field of AWG have mainly dealt with the condensation of humidity on cold surfaces with a cooling system or with absorption and thermal desorption. In this paper, another possibility for AWG is investigated, specifically AWG using absorption and reverse osmosis. For this purpose, models have been set up for an absorber operated in countercurrent and reverse osmosis membrane modules operated in co-current and countercurrent. With these models, simulations with different boundary conditions were then carried out using the programming language Python. The simulations have shown that the reverse osmosis membrane modules operated in countercurrent generally have a lower energy demand and require fewer reverse osmosis stages than those operated in co-current.

Keywords: absorption; reverse osmosis; heat transfer; mass transfer; process modeling; air water generation; modeling; simulation

1. Introduction

Water shortage is a global issue. Competition for fresh water is expected to intensify further as a result of increasing population and climate change [1]. Not only arid regions such as Northern Africa or the Middle East but also, for example, Central and Mediterranean Europe are increasingly affected [2]. According to the World Health Organization and Unicef, half of the world's population will be living in water-stressed areas by 2025, and only approximately 80% of the world's population will have access to safe drinking water at home by 2030, leaving 1.6 billion people without [3]. Physically, there is enough fresh liquid water on the earth's surface in the form of lakes and rivers to supply humankind. This amount corresponds to a volume of about 90,000 km³ [4]. However, there are many regions without sufficient natural drinking water resources. In regions where access to seawater or polluted water is available, desalination or wastewater treatment plants can be used to provide clean water [5]. In case seawater is available, reverse osmosis with membranes is normally used due to the high energy efficiency [6]. If no access to liquid water exists, the water must be transported to the recipients by land or air. In many regions affected by water shortages, large facilities that provide clean water in sufficient quantities do not exist, and transport by land or air seems not feasible. Another potential source is the atmosphere, where the water is stored in the form of water vapor. The earth's atmosphere contains so much water vapor that in its liquid state it would have a volume of about 13,000 km³, which is about one seventh the volume of fresh water on the earth's surface [4].

In order to extract water from the atmosphere, currently either the condensation of air humidity on cold surfaces with a cooling system or sorption with classical desorption

(especially by increasing the temperature) is used [7,8]. However, these processes are very energy-intensive. One possible alternative is the combination of two established processes, absorption and reverse osmosis. With a salt solution, water is extracted from the ambient air and subsequently expelled from the aqueous salt solution using multiple reverse osmosis stages instead of desorption. Fill et al. have shown the feasibility of water extraction from the ambient air using this combination [9]. The results in terms of specific energy demand were promising but roughly comparable to those of conventional processes. This makes it necessary to improve the level of detail of the modeling and to investigate process variants. In this way, it can be clarified whether there is potential for savings so that the process can stand out from conventional processes. In the modeling, all state and process variables as well as all key figures are to be recalculated for each finite element. Furthermore, the reverse osmosis process is to be run in countercurrent operation in order to increase the average difference of the chemical potential and thus the water flow through the membranes.

2. Materials and Methods

2.1. Absorbents

The absorbent utilized in the two sub-processes, absorption and reverse osmosis, has to meet specific requirements. However, these requirements are in direct conflict with one another. On the one hand, the mass fraction of the solute must be maximal to exhibit low water vapor partial pressures in order to absorb enough water vapor from the air, and on the other hand, the mass fraction of the solute must be minimal for low osmotic pressures. For this reason, a variety of different absorbents were evaluated, with aqueous salt solutions containing lithium bromide (LiBr), lithium chloride (LiCl), sodium hydroxide (NaOH), and potassium hydroxide (KOH) proving to be particularly effective. Lithium bromide was eventually chosen for the further investigations because it can attain the lowest water vapor partial pressures and has the lowest toxicity values [9].

2.2. Conceptual Design of Reverse Osmosis Based Air Water Generator

Conventional reverse osmosis membrane modules have no inlet on the permeate side and can usually only be operated up to a maximal pressure of about 120 bar [10]. Since osmotic pressures of up to 2000 bar have to be overcome for salt solutions with salt mass fractions of up to $w \approx 0.5$, Fill et al. presented a configuration that still allows reverse osmosis to be used [9]. In order to reduce the osmotic pressure, an inlet is added on the permeate side, where a salt solution of lower concentration than in the feed is introduced. Figure 1 shows an exemplary representation of this configuration. The slightly lower concentrated permeate of the first module enters the second module as feed and the retentate of the second module is subsequently reintroduced into the first module as permeate inlet.

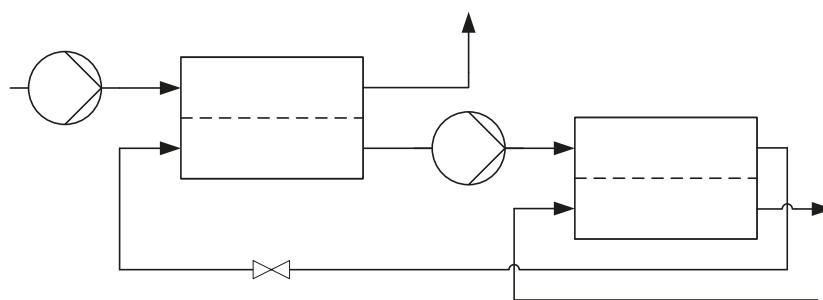


Figure 1. Multi-stage reverse osmosis [9].

This configuration reduces the osmotic pressure across the membrane, which can be calculated from the chemical potential using the following Equation [11] p. 306.

$$\Pi = p_2 - p_1 = -\frac{RT}{\tilde{V}_j} \ln \frac{a_{j,2}}{a_{j,1}} = -\frac{RT}{\tilde{V}_j} \ln \frac{x_{j,2} \gamma_{j,2}}{x_{j,1} \gamma_{j,1}} \quad (1)$$

This modification distributes the osmotic pressure over several modules, but the total pressure to be applied remains the same and thus also the required pump energy. Therefore, pressure exchangers (PX) are used to recover part of the pressure energy. Their efficiency can be calculated as follows.

$$\eta_{PX} = \frac{\sum (p \dot{V})_{out}}{\sum (p \dot{V})_{in}} \quad (2)$$

Pressure exchangers are commonly used in seawater reverse osmosis processes and have an efficiency of up to 95% [12]. By using such pressure exchangers, booster pumps are no longer necessary before each module, employing a booster pump once the pressure falls below a certain limit is sufficient. As a result, there is a massive reduction in the total pressure that must be exerted with pumps.

2.2.1. Co-Current Multi-Stage Reverse Osmosis

Figure 2 shows the schematic of the entire process for an arbitrary number of co-current reverse osmosis membrane modules. A pressure exchanger is placed between each successive pair of reverse osmosis membrane modules. Additionally, one is placed between the second last and first membrane module, which leads to a significant reduction in the overall energy demand of the pumps.

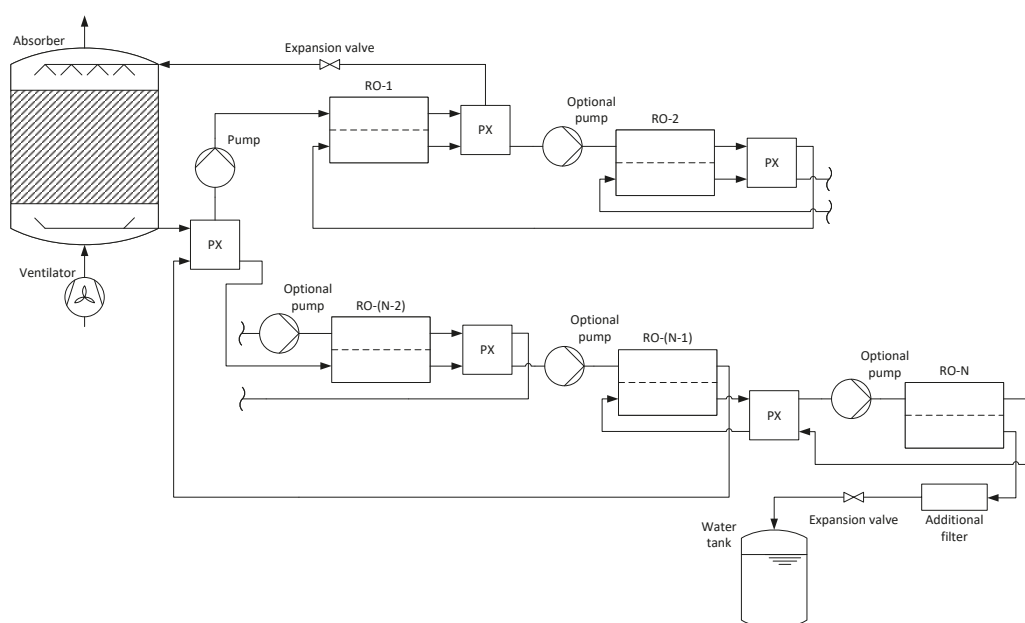


Figure 2. Process schematic for an AWG with absorption and co-current multi-stage reverse osmosis from [9].

2.2.2. Countercurrent Multi-Stage Reverse Osmosis

Figure 3 shows the schematic of the entire process for an arbitrary number of countercurrent reverse osmosis membrane modules. As with the co-current process, a pressure exchanger is placed between two successive and between the second last and first membrane module to reduce the overall energy demand of the pumps.

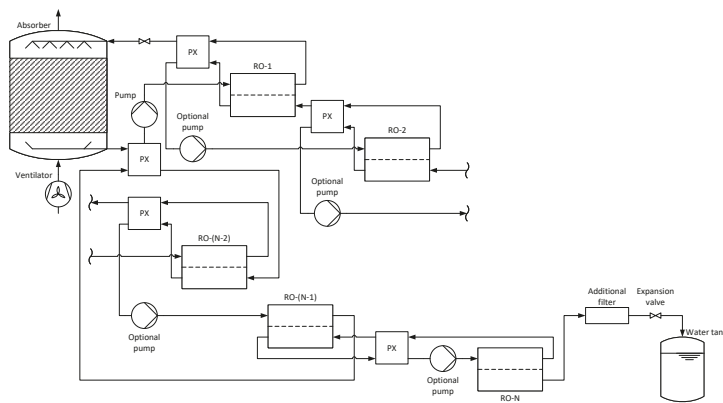


Figure 3. Process schematic for an AWG with absorption and countercurrent multi-stage reverse osmosis.

2.3. Modeling

The following models are all assuming steady state operation. The thermodynamic properties of the aqueous lithium bromide solution are determined using Hirschberg's mathematical fits [13] pp. 788–789. For certain transport properties, mathematical fits of an engineering equation solver from the University of Maryland were used [14]. The vapor pressures of water are calculated using the Antoine Equation [15] p. 439.

2.3.1. Absorber

The absorber is modeled as a falling film absorber, with thin plates arranged side by side providing the surface for the down-flowing salt solution. Air flows into the absorber from the bottom and flows along the salt solution towards the upper end of the absorber; thus the air and the salt solution are in countercurrent flow.

Assumptions

To model the absorber, the following simplifying assumptions were made:

- The pressure p in the aqueous lithium bromide solution is constant.
- The total pressure p_{tot} of the air is constant.
- The liquid film is flat and has no surface waves.
- The film thickness is considered constant along the height of the absorber column.
- The inlet mass flow rate of the solution and the inlet volume flow rate of the air are assumed to be constant and are calculated according to Appendices B and C of [9].
- The conditions of the air and solution are constant at a given height of the absorber.

These assumptions simplify the model significantly. For a more accurate model, which, however, would also require significant more computational power, the absorber could be discretized in two dimensions or the influence of wave dynamics could be included [16,17].

Correlations

In the absorber, a turbulent air flow is desired. According to the VDI Heat Atlas, the Nusselt number for a plane gap with turbulent flow ($Re > 3 \times 10^4$) can be calculated with the following correlation [18] p. 807.

$$\zeta = (1.8 \log_{10}(Re) - 1.5)^{-2}$$

$$Nu = \frac{(\zeta/8)(Re - 1000) Pr}{1 + 12.7 \sqrt{\zeta/8} (Pr^{2/3} - 1)} \left[1 + \frac{1}{3} \left(\frac{d_h}{x} \right)^{2/3} \right] \quad (3)$$

The hydraulic diameter d_h for a plane gap is defined as $d_h = 2s$, where s is the gap thickness. By calculating the Nusselt number at each position x in the absorber, position-dependent heat and mass transfer coefficients are obtained.

Calculations of the Absorber

The absorber is divided into a finite number of elements i and for each of these elements the following calculations are performed.

Before performing the heat and mass transfer calculations, the dry air mass flow rate of the incoming moist air must be calculated, as it is constant throughout the absorber.

$$\dot{m}_{a,dry} = (p_{tot} - p_w) \frac{\dot{V}_a}{R_a T_a} = \text{const.} \quad (4)$$

p_{tot} is the total pressure and p_w is the water vapor partial pressure of the air.

Similar to the mass flow rate of the dry air, the salt mass flow rate in the absorber remains constant.

$$\dot{m}_{LiBr} = \dot{m}_{sol} w_{LiBr} = \text{const.} \quad (5)$$

The previously calculated Nusselt number can now be used to calculate the heat transfer coefficient α_i and therefore the heat flow $\dot{Q}_i$.

$$\dot{Q}_i = \alpha_i A_i (T_{a,i} - T_{sol,i}) \quad (6)$$

The water mass flow $\dot{m}_{w,i}$ absorbed by the salt solution is calculated with the mass transfer coefficient β_i , which is defined by the dimensionless Lewis number (approximately 1 for an air–water vapor mixture [18] p. 1945).

$$\dot{m}_{w,i} = \beta_i A_i \rho (X_{a,i} - X_{a,i}^{vap}) \quad (7)$$

Therein, $X_{a,i}^{vap}$ is the mass load over the salt solution in kg of water per kg of dry air. With the water mass flow rate $\dot{m}_{w,i}$, the enthalpy flow $\dot{H}_i$ can then be calculated.

$$\dot{H}_i = \dot{m}_{w,i} (\Delta h_v + \vartheta_{a,i} c_{p,vap}) \quad (8)$$

With the dry air mass flow rate, heat flow, and enthalpy flow, the energy balance for the air can now be set up and solved for each element i .

$$\dot{m}_{a,dry} (h_{a,i+1} - h_{a,i}) - \dot{Q}_i - \dot{H}_i = 0 \quad (9)$$

Analogously, the energy balance for the salt solution is also set up and solved for each element i .

$$\dot{m}_{sol,i} (h_{sol,i-1} - h_{sol,i}) + \dot{Q}_i + \dot{H}_i = 0 \quad (10)$$

Further, the mass balance for the air is set up and solved for each element i .

$$\dot{m}_{a,dry} (X_{a,i+1} - X_{a,i}) - \dot{m}_{w,i} = 0 \quad (11)$$

Analogously, as with the energy balance, the same is done for the salt solution.

$$\dot{m}_{LiBr} (X_{sol,i-1} - X_{sol,i}) + \dot{m}_{w,i} = 0 \quad (12)$$

In Equations (11) and (12), X_a and X_{sol} denote the mass loads in kg of water per kg of dry air and kg of water per kg of LiBr, respectively.

Calculations of the Ventilator

The required electrical power of the ventilator is determined by the pressure losses in the absorber. They can be calculated using the following equation.

$$\Delta p = \zeta \frac{l}{d_h} \frac{\rho v^2}{2} \quad (13)$$

According to Blasius, the drag coefficient ζ used therein can be calculated for turbulent flows as follows [18] p. 1356.

$$\zeta = \frac{0.3164}{\sqrt[4]{Re}} \quad (14)$$

Solution Algorithm

In the solution algorithm, the inlet salt mass fraction and temperature are first assumed. The inlet temperature of the absorber is then adjusted until it matches the outlet temperature and therefore steady state is reached. Subsequently, the inlet salt mass fraction is adjusted until the desired amount of water is absorbed, i.e., the target water output.

2.3.2. Reverse Osmosis Process

The reverse osmosis membrane modules are modeled for co-current and countercurrent flow.

Assumptions

For the models of the reverse osmosis membrane modules, the following simplifying assumptions were made:

- No temperature changes over the membranes, the pressure exchangers or the pumps.
- The membrane has a salt rejection of 100%, so no salt flows through the membrane.
- Concentration polarization phenomena in the membrane are not considered.
- Water mass transfer through the membrane is calculated using a membrane constant.
- The representative membrane module used has a pressure drop of 1 bar; therefore, this pressure drop is distributed linearly over the membrane.
- No leakages between the streams in the pressure exchangers.

The membrane of the reverse osmosis membrane module can be modeled with different levels of detail. However, in this work, with the assumptions made previously, the model is simplified. For a more accurate model, which would require more computational power, for example, mass transfer in the membrane could be calculated using the solution–diffusion model, a solute permeability coefficient could be included, or concentration polarization phenomena could be included [19–21].

Calculations of the Reverse Osmosis Membrane Modules

Before the calculations for the reverse osmosis membrane modules can be performed, the membrane constant A_{memb} must be determined. This can be done using water fluxes specified by the manufacturer under standard conditions [22]. In this model, a representative module from DuPont de Nemours, Inc. was chosen [10].

$$A_{memb} = \frac{J_w}{\Delta p - \Pi} \quad (15)$$

Subsequently, the calculations are performed for each element i . Since the membrane constant is known, the water flow through the membrane can be calculated:

$$\dot{m}_{w,i} = A_{memb} A_i (\Delta p_i - \Pi_i) \quad (16)$$

where A_i is the exchange area, Δp_i the transmembrane pressure difference between feed and permeate, and Π_i the osmotic pressure, according to Equation (1), of the i -th element. Then the mass flow rate of LiBr in the feed is calculated, which is assumed to be constant since only water passes through the membrane.

$$\dot{m}_{LiBr,f} = \dot{m}_f w_{LiBr,f} = \text{const.} \quad (17)$$

The same applies to the mass flow rate of LiBr in the permeate, which is also constant.

$$\dot{m}_{LiBr,p} = \dot{m}_p w_{LiBr,p} = \text{const.} \quad (18)$$

With the mass flow rate of LiBr in the feed, the mass balance on the feed side can be set up and solved for each element i .

$$\dot{m}_{LiBr,f} (X_{f,i-1} - X_{f,i}) - \dot{m}_{w,i} = 0 \quad (19)$$

Analogously, the mass balance on the permeate side can be set up with the mass flow rate of LiBr in the permeate and solved for each element i . For the reverse osmosis membrane module operated in co-current, this results in the following equation.

$$\dot{m}_{LiBr,p} (X_{p,i-1} - X_{p,i}) + \dot{m}_{w,i} = 0 \quad (20)$$

Similarly, the following mass balance is obtained for the countercurrent reverse osmosis membrane module.

$$\dot{m}_{LiBr,p} (X_{p,i+1} - X_{p,i}) + \dot{m}_{w,i} = 0 \quad (21)$$

In Equations (19)–(21), X denotes the mass load in kg of water per kg of LiBr of the respective membrane side.

Calculations of the Pressure Exchangers and Pumps

According to Equation (2), the pressure recovered by the pressure exchanger, respectively, the pressure of the next reverse osmosis module p_f can be calculated as follows.

$$p_f = \eta_{PX} (p_r + p_{p,out}) - p_{p,in} \quad (22)$$

In the previous equation, η_{PX} is the efficiency of the pressure exchanger, p_r the high pressure retentate leaving the previous module, $p_{p,out}$ the low pressure permeate leaving the previous module and $p_{p,in}$ the entering permeate pressure of the previous module.

To calculate the electric power P_{el} of the pump, the hydraulic power P_h and its total efficiency η_{tot} are needed.

$$P_{el} = \frac{P_h}{\eta_{tot}} = \frac{\dot{V}_{sol} \Delta p}{\eta_{tot}} \quad (23)$$

The hydraulic power P_h of the pump can be calculated from the volume flow rate $\dot{V}_{sol}$ of the solution and the required pressure increase Δp [23] p. 48.

Solution Algorithm

In the solution algorithm, a salt mass fraction is assumed at the permeate inlet for each reverse osmosis membrane module. Subsequently, this inlet permeate salt mass fraction is adjusted until the osmotic pressure is at a level where the desired amount of water flows through the membrane, i.e., the target water output. A new membrane module is then added, where the inlet salt mass fraction is again adjusted until the desired amount of water flows through the membrane. This is repeated until the osmotic pressure is sufficiently low for pure water to be on the permeate side. Then a conventional reverse osmosis membrane module is added, which has no inlet on the permeate side. Since, due

to pressure losses, the available feed pressure at the inlet of a new membrane module steadily decreases, a booster pump is used to increase the pressure as soon as it falls below a certain critical value.

2.4. Simulations

The systems modeled according to Section 2.3 were simulated in Python [24]. A water output of 500 L/d, an air volume flow rate of 40,000 m³/h, and a solution mass flow of 1.5 kg/s were used as input parameters. Furthermore, different values for the partial pressure of water vapor p_w and the ambient air temperature T_{air} were used as boundary conditions for a series of simulations.

For the geometry of the heat and mass transfer area in the absorber, a rectangular cross-section with a height of 3 m, a width of 2 m, and 20 gaps with a gap thickness of 0.05 m were used. For the defined boundary conditions, Equation (13) yields pressure losses Δp of approximately 15 Pa, which corresponds to a required electrical power of 800 W for the specified air volume flow rate [25].

The membrane constant A_{memb} of the used membrane module, which is calculated using Equation (15) and is required for the calculations of the membrane modules, is 3.402×10^{-9} kg/(s m² Pa).

The simulations were carried out for an AWG system with either co-current or countercurrent operated reverse osmosis membrane modules using either a fixed booster pump pressure of $p = 100$ bar or a variable booster pump pressure. With the former, a booster pump is allotted when the pressure drops below 100 bar, and with the latter, the pressure of the booster pump is adjusted to reduce the energy demand per cubic meter of water.

3. Results

3.1. Co-Current Multi-Stage Reverse Osmosis

In Figure 4, the results of the different simulation series for the AWG with co-current operated reverse osmosis membrane modules are shown. The figures on the left side (Figure 4a,c) show the energy demands per cubic meter of water and the figures on the right side (Figure 4b,d) show the number of necessary reverse osmosis membrane modules. The upper ones, Figure 4a,b, are for a fixed booster pump pressure and the lower ones, Figure 4c,d, for variable. At low water vapor partial pressures and high temperatures, the values for the energy demand and the number of modules are both the highest and decrease with increasing water vapor partial pressure and decreasing temperature. The energy demands with the variable booster pump pressure are either equal to or smaller than those with the fixed booster pump pressure.

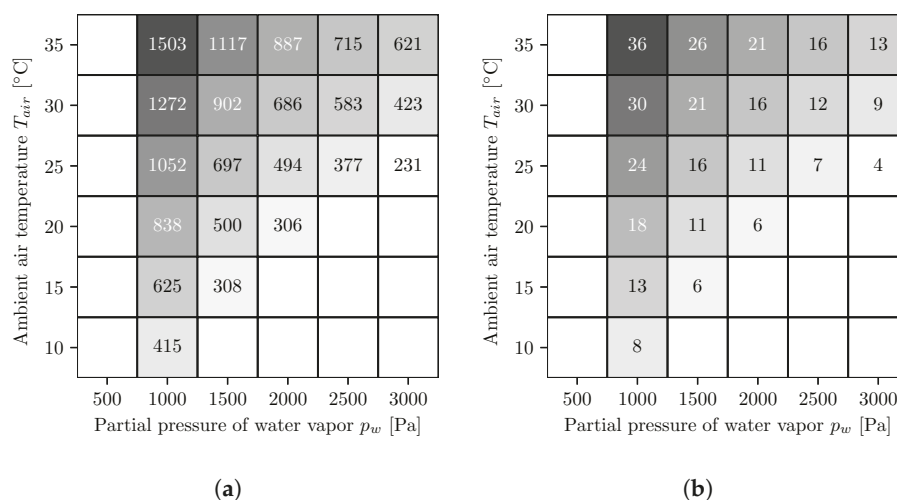


Figure 4. Cont.

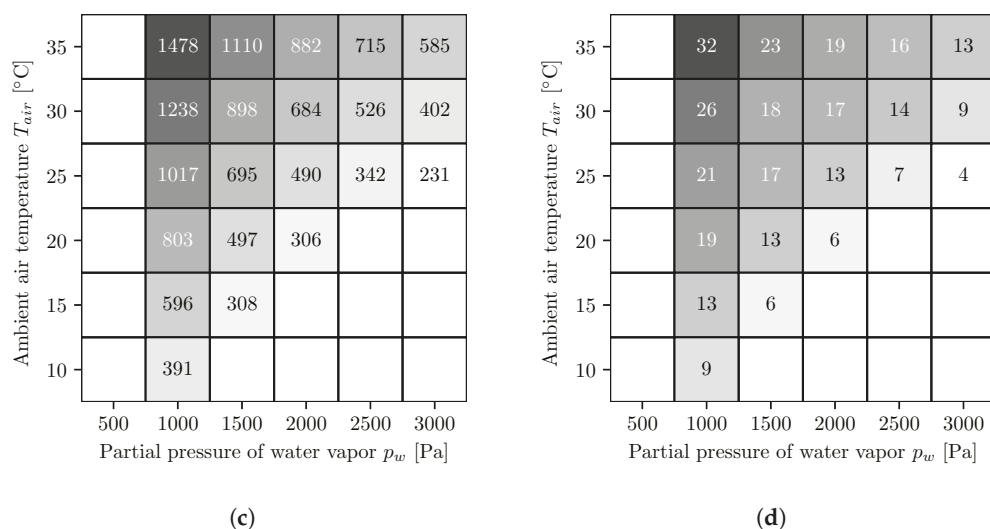


Figure 4. Energy demand per cubic meter of water [kWh/m³] (a,c) and number of necessary reverse osmosis membrane modules (b,d) for fixed (a,b) and optimized (c,d) booster pump pressure. The following applies to all figures. The white areas on the left side represent conditions where, for the chosen absorber dimensions, not enough water can be extracted from the air because the required salt mass fraction is too high and the solution starts to crystallize. To determine whether the solution begins to crystallize, the solid liquid equilibrium of aqueous lithium bromide is used [26]. The white areas in the lower right corners represent conditions where the air is oversaturated and therefore no representative statements can be made.

3.2. Countercurrent Multi-Stage Reverse Osmosis

In Figure 5, the results of the different simulation series for the AWG with countercurrent operated reverse osmosis membrane modules are shown. The figures on the left side (Figure 5a,c) show the energy demands per cubic meter of water, and the figures on the right side (Figure 5b,d) show the number of necessary reverse osmosis membrane modules. The upper ones, Figure 5a,b, are for a fixed booster pump pressure, and the lower ones, Figure 5c,d, for variable. As with co-current, the values for energy demand and number of modules are highest at low water vapor partial pressures and high temperatures and decrease with increasing water vapor partial pressure and decreasing temperature. Likewise, the energy demands with the variable booster pump pressure are either equal to or smaller than the values with the fixed booster pump pressure. Furthermore, the energy demands are smaller compared to the co-current.

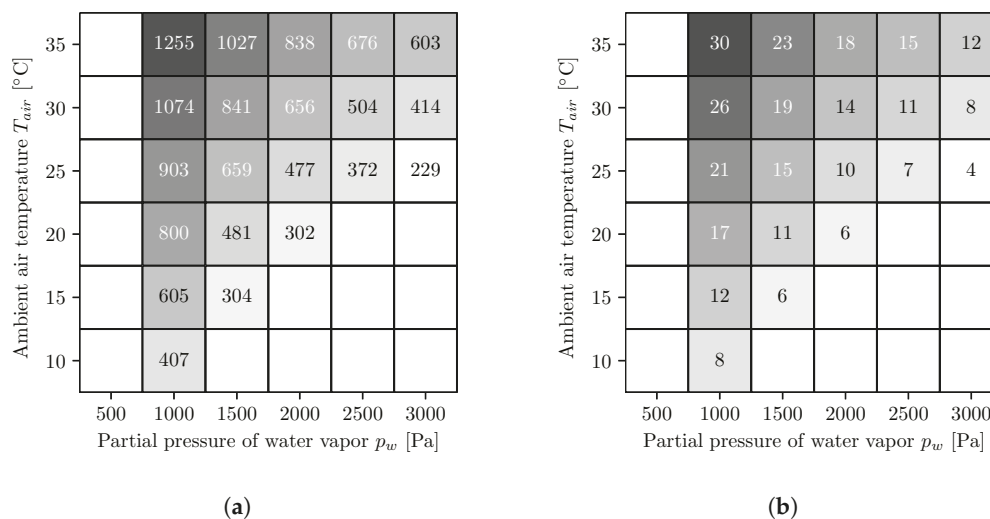


Figure 5. Cont.

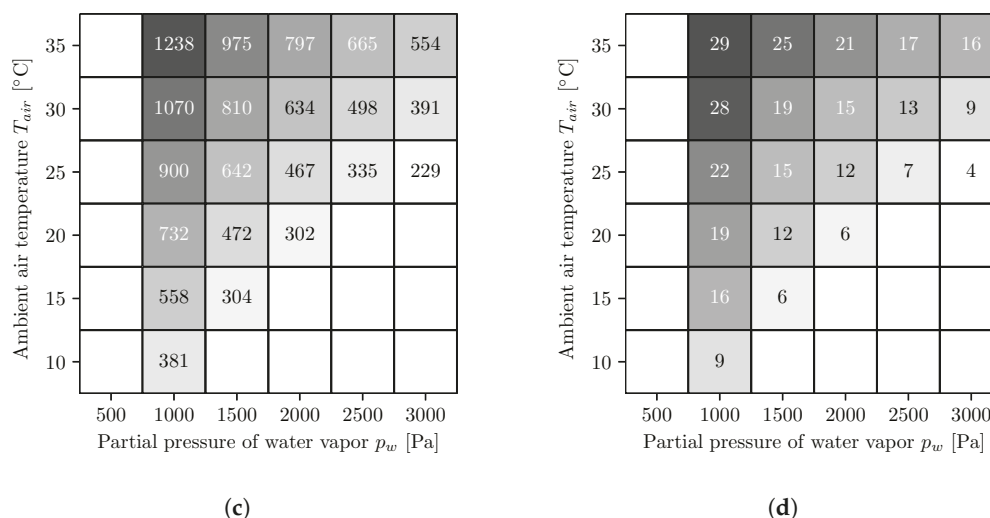


Figure 5. Energy demand per cubic meter of water (kWh/m^3) (a,c) and number of necessary reverse osmosis membrane modules (b,d) for fixed (a,b) and optimized (c,d) booster pump pressure. The following applies to all figures. The white areas on the left side represent conditions where, for the chosen absorber dimensions, not enough water can be extracted from the air because the required salt mass fraction is too high and the solution starts to crystallize. To determine whether the solution begins to crystallize, the solid liquid equilibrium of aqueous lithium bromide is used [26]. The white areas in the lower right corners represent conditions where the air is oversaturated and therefore no representative statements can be made.

4. Discussion

In the present paper, AWG systems based on absorption and reverse osmosis were investigated in terms of specific energy demand. The absorber was modeled in counter-current, whereby the state and process variables as well as the key figures were calculated in each finite element, and the reverse osmosis process was modeled for both co-current and countercurrent operations. Subsequently, these models were combined to systems and used to perform simulations. The simulations were performed for co-current and countercurrent reverse osmosis membrane modules, both with fixed and variable booster pump pressure.

The results of the simulations show similar energy demands for all variants. In the case of co-current reverse osmosis membrane modules and fixed booster pump pressures, the specific energy demand is between ~ 230 – $1500 \text{ kWh}/\text{m}^3$, and for co-current operation with variable booster pump pressures, it is between ~ 230 – $1480 \text{ kWh}/\text{m}^3$. For countercurrent operation with fixed booster pump pressures, the specific energy demand is between ~ 230 – $1260 \text{ kWh}/\text{m}^3$, and for countercurrent operation with variable booster pump pressures, it is between ~ 230 – $1240 \text{ kWh}/\text{m}^3$. The simulations with variable booster pump pressures resulted in energy demands that were equal to or smaller than those with fixed booster pump pressures; however, they required more reverse osmosis membrane module stages. Under ideal conditions, the values simulated in this paper are slightly lower than those determined by Wahlgren for condensation processes, which require between 270 and $550 \text{ kWh}/\text{m}^3$ [27].

Generally, this work has shown that an AWG with absorption and countercurrent reverse osmosis membrane modules is more efficient than one with co-current operation, but under favorable boundary conditions, this has no significant impact on the energy demand. The efficiency of the systems could be further improved, for example, by optimizing the geometries of the components. In the models of the reverse osmosis membrane modules, a salt rejection of 100% was assumed. As this does not apply for real membranes, it should be investigated how strongly salt permeation affects the number of modules and thus the energy demand. In addition, experiments should be carried out to determine whether manufacturing and operating such reverse osmosis membrane mod-

ules is possible. Another aspect that has not been considered in this paper is the economic aspect. Therefore, the levelized cost of water (LCOW) should be calculated, i.e., the ratio between the sum of lifetime costs and the sum of lifetime produced water [28]. Next, the LCOW of the process presented in this paper can be compared with other comparable processes and evaluated economically. In addition, further simulations can be carried out with the other previously mentioned absorbents to compare their LCOW with each other.

Author Contributions: Conceptualization, M.F. and M.K.; methodology, M.F. and M.K.; software, M.F.; validation, M.F. and M.K.; formal analysis, M.F. and M.K.; investigation, M.F.; resources, M.F.; data curation, M.F.; writing—original draft preparation, M.F.; writing—review and editing, M.F. and M.K.; visualization, M.F.; supervision, M.K.; project administration, M.K.; funding acquisition, M.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors would like to thank the Albert Koechlin Stiftung for funding an initial project that laid the foundation for this work.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

Abbreviations

AWG	Air water generator/air water generation
LCOW	Levelized cost of water
PX	Pressure exchanger

Symbols

a	Activity [—]
A	Area [m^2]
A_{memb}	Membrane constant [$\text{kg}/(\text{s m}^2 \text{ Pa})$]
c	Concentration [mol/m^3]
c_p	Specific heat capacity (at constant pressure) [$\text{J}/(\text{kg K})$]
d	Diameter [m]
D	Diffusion coefficient [m^2/s]
h	Specific enthalpy [J/kg]
$\dot{H}$	Enthalpy flow [W]
J	Mass flux [$\text{kg}/(\text{s m}^2)$]
L_{char}	Characteristic length [m]
$\dot{m}$	Mass flow rate [kg/s]
N	Number of elements [—]
p	Pressure [Pa]
P	Power [W]
$\dot{Q}$	Heat flow [W]
R	Universal gas constant [$\text{J}/(\text{mol K})$]
s	Gap thickness [m]
T	Temperature [K]
$vs.$	Velocity [m/s]
V	Volume [m^3]
$\tilde{V}$	Molar volume [m^3/mol]
$\dot{V}$	Volume flow rate [m^3/s]
w_i	Mass fraction of component i [kg/kg]
x	Position [m]
x_i	Mole fraction of component i [mol/mol]
X_i	Mass load of water per component i [kg/kg]

Indices

<i>a</i>	Air
<i>abs</i>	Absorption
<i>avg</i>	Average
<i>el</i>	Electric
<i>elem</i>	Element
<i>f</i>	Feed
<i>g</i>	Gas
<i>h</i>	Hydraulic
<i>i</i>	<i>i</i> -th element
<i>in</i>	Inlet
<i>j</i>	Solvent
<i>out</i>	Outlet
<i>p</i>	Permeate
<i>r</i>	Retentate
<i>sol</i>	Solution
<i>tot</i>	Total
<i>vap</i>	Vapor
<i>w</i>	Water

Greek Symbols

α	Heat transfer coefficient [W/(m ² K)]
β	Mass transfer coefficient [m/s]
γ	Activity coefficient [–]
δ	Film thickness [m]
ζ	Drag coefficient [–]
η	Efficiency [–]
θ	Temperature [°C]
λ	Thermal conductivity [W/(m K)]
μ	Chemical potential [J/mol]
ν	Kinematic viscosity [m ² /s]
ρ	Density [kg/m ³]
Π	Osmotic pressure [Pa]

Dimensionless Numbers

$Le = \lambda / (D \rho c_p)$	Lewis number
$Nu = \alpha L_{char} / \lambda$	Nusselt number
$Pr = \nu \rho c_p / \lambda$	Prandtl number
$Re = \rho v L_{char} / \eta$	Reynolds number

References

1. IPCC. Summary for Policymakers. In *Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*; Masson-Delmotte, V., Zhai, P., Pirani, A., Connors, S.L., Péan, C., Berger, S., Caud, N., Chen, Y., Goldfarb, L., Gomis, M.I., et al., Eds.; Cambridge University Press: Cambridge, UK, 2021.
2. Markonis, Y.; Kumar, R.; Hanel, M.; Rakovec, O.; Máca, P.; AghaKouchak, A. The rise of compound warm-season droughts in Europe. *Sci. Adv.* **2021**, *7*, eabb9668. [CrossRef]
3. *Progress on Household Drinking Water, Sanitation and Hygiene 2000–2020: Five Years into the SDGs*; Report; World Health Organization (WHO): Geneva, Switzerland; United Nations Children's Fund (UNICEF): Geneva, Switzerland, 2021.
4. Shiklomanov, I. *Water in Crisis: A Guide to the World's Fresh Water Resources*; Chapter World Fresh Water Resources; Oxford University Press: New York, NY, USA, 1993.
5. Baker, R.W. *Membrane Technology and Applications*; J. Wiley: Chichester, UK, 2004.
6. Zheng, X.; Wen, J.; Shi, L.; Cheng, R.; Zhang, Z. A top-down approach to estimate global RO desalination water production considering uncertainty. *Desalination* **2020**, *488*, 114523. [CrossRef]
7. Mirmanto, M.; Syahrul, S.; Wijayanta, A.; Mulyanto, A.; Winata, L. Effect of evaporator numbers on water production of a free convection air-water harvester. *Case Stud. Therm. Eng.* **2021**, *27*, 101253. [CrossRef]
8. Li, R.; Shi, Y.; Wu, M.; Hong, S.; Wang, P. Improving atmospheric water production yield: Enabling multiple water harvesting cycles with nano sorbent. *Nano Energy* **2020**, *67*, 104255. [CrossRef]

9. Fill, M.; Muff, F.; Kleingries, M. Evaluation of a new air water generator based on absorption and reverse osmosis. *Heliyon* **2020**, *6*, e05060. [CrossRef] [PubMed]
10. DuPont de Nemours, Inc. DuPont™XUS180808 Reverse Osmosis Element. 2020. Available online: <https://www.dupont.com/content/dam/dupont/amer/us/en/water-solutions/public/documents/en/45-D01736-en.pdf> (accessed on 8 March 2021).
11. Kraume, M. *Transportvorgänge in der Verfahrenstechnik*; Springer: Berlin/Heidelberg, Germany, 2012. [CrossRef]
12. Cameron, I.B.; Clemente, R.B. SWRO with ERI's PX Pressure Exchanger device—A global survey. *Desalination* **2008**, *221*, 136–142. [CrossRef]
13. Hirschberg, H.G. *Handbuch Verfahrenstechnik und Anlagenbau*; Springer: Berlin/Heidelberg, Germany, 2014.
14. University of Maryland. LiBrSSC (Aqueous Lithium Bromide) Property Routines. Available online: http://fchart.com/ees/libr_help/ssclibr.pdf (accessed on 6 December 2019).
15. Rönsch, S. *Anlagenbilanzierung in der Energietechnik*; Springer: Wiesbaden, Germany, 2015; doi:10.1007/978-3-658-07824-9. [CrossRef]
16. Bo, S.; Ma, X.; Lan, Z.; Chen, J.; Chen, H. Numerical simulation on the falling film absorption process in a counter-flow absorber. *Chem. Eng. J.* **2010**, *156*, 607–612. [CrossRef]
17. Xu, Z.F.; Khoo, B.C.; Wijeyesundera, N.E. Mass transfer across the falling film: Simulations and experiments. *Chem. Eng. Sci.* **2008**, *63*, 2559–2575. [CrossRef]
18. Stephan, P.; Kabelac, S.; Kind, M.; Mewes, D.; Schaber, K.; Wetzel, T. (Eds.) *VDI-Wärmeatlas*; Springer: Berlin/Heidelberg, Germany, 2019; doi:10.1007/978-3-662-52989-8. [CrossRef]
19. Thomas Melin, R.R. *Membranverfahren*; Springer: Berlin/Heidelberg, Germany, 2007.
20. Jiang, A.; Ding, Q.; Wang, J.; Jiangzhou, S.; Cheng, W.; Xing, C. Mathematical Modeling and Simulation of SWRO Process Based on Simultaneous Method. *J. Appl. Math.* **2014**, *2014*, 908569. [CrossRef]
21. Sundaramoorthy, S.; Srinivasan, G.; Murthy, D.V.R. An analytical model for spiral wound reverse osmosis membrane modules: Part I—Model development and parameter estimation. *Desalination* **2011**, *280*, 403–411. [CrossRef]
22. Moser, M.; Micari, M.; Fuchs, B.; Farnós, J. *Software Tool for the Simulation of Selected Brine Treatment Technologies*; Technical Report; Horizon 2020 Framework Programme: Delft, The Netherlands, 2018.
23. Böswirth, L.; Bschorer, S. *Technische Strömungslehre*; Springer: Wiesbaden, Germany, 2014; doi:10.1007/978-3-658-05668-1. [CrossRef]
24. Van Rossum, G.; Drake, F.L. *Python 3 Reference Manual*; CreateSpace: Scotts Valley, CA, USA, 2009.
25. Vostermans Ventilation. Fiberglass Cone Fans—Efficient Ventilation with High Air Yields. 2020. Available online: <https://www.vostermans.com/hubfs/Brochures/Fans/Fiberglass%20Cone%20Fans/Multifan%20Fiberglass%20Cone%20fan%20EN.pdf?hsLang=en> (accessed on 8 March 2021).
26. Conde-Petit, M.R. Solid—Liquid Equilibria (SLE) and Vapour—Liquid Equilibria (VLE) of Aqueous LiBr. 2014. Available online: <http://www.aldacs.com/DocBase/AqLiBrSLEVLE.pdf> (accessed on 6 December 2019).
27. Wahlgren, R.V. Atmospheric water vapour processor designs for potable water production: A review. *Water Res.* **2001**, *35*, 1–22. [CrossRef]
28. Leiva-Illanes, R.; Escobar, R.; Cardemil, J.M.; Alarcón-Padilla, D.C. Comparison of the levelized cost and thermoeconomic methodologies—Cost allocation in a solar polygeneration plant to produce power, desalted water, cooling and process heat. *Energy Convers. Manag.* **2018**, *168*, 215–229. [CrossRef]



Article

Model Evaluation of the Microbial Metabolic Processes in a Hydrogen-Based Membrane Biofilm Reactor for Simultaneous Bromate and Nitrate Reduction

Minmin Jiang ^{1,2}, Yuanyuan Zhang ², Jie Zhang ^{2,3,4}, Xingru Dai ², Haixiang Li ^{1,*}, Xuehong Zhang ^{1,2}, Zhichao Wu ⁴ and Junjian Zheng ^{2,4,*}

¹ Guangxi Key Laboratory of Environmental Pollution Control Theory and Technology, Guilin University of Technology, 319 Yanshan Street, Guilin 541006, China

² College of Life and Environmental Science, Guilin University of Electronic Technology, 1 Jinji Road, Guilin 541004, China

³ School of Chemistry and Materials Engineering, Huizhou University, 46 Yanda Road, Huizhou 516007, China

⁴ State Key Laboratory of Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Tongji University, 1239 Siping Road, Shanghai 200092, China

* Correspondence: 2011042@glut.edu.cn (H.L.); zhengjunjianglut@163.com (J.Z.)

Abstract: The H₂-based membrane biofilm reactor (H₂-MBfR) has been acknowledged as a cost-effective microbial reduction technology for oxyanion removal from drinking water sources, but it remains unknown how the evolution of biofilm characteristics responds to the changing critical operating parameters of the H₂-MBfR for simultaneous bromate (BrO₃[−]) and nitrate (NO₃[−]) elimination. Therefore, an expanded multispecies model, applicable to mechanistically interpret the bromate-reducing bacteria (BRB)- and denitrifying bacteria (DNB)-dominated metabolic processes in the biofilm of the H₂-MBfR, was developed in this study. The model outputs indicate that (1) increased BrO₃[−] loading facilitated the metabolism of BRB by increasing BRB fraction and BrO₃[−] gradients in the biofilm, but had a marginal influence on NO₃[−] reduction; (2) H₂ pressure of 0.04 MPa enabled the minimal loss of H₂ and the extension of the active region of BRB and DNB in the biofilm; (3) once the influent NO₃[−] concentration was beyond 10 mg N/L, the fraction and activity of BRB significantly declined; (4) BRB was more tolerant than DNB for the acidic aquatic environment incurred by the CO₂ pressure over 0.02 MPa. The results corroborate that the degree of microbial competition for substrates and space in the biofilm was dependent on system operating parameters.

Keywords: BrO₃[−]; NO₃[−]; bioreactor; microbial reduction; multispecies model; biofilm characteristics

1. Introduction

Bromate (BrO₃[−]), a common disinfection byproduct formed during the advanced oxidation processes (especially ozonation) of drinking water, has been assigned as a Group 2B carcinogen with a maximum contaminant level of 10 µg/L in potable water by the World Health Organization [1–3]. The BrO₃[−] concentration varies typically from below 30 µg/L in the ozonated surface water to 0.8–1.4 mg/L in the groundwater intruded by industrial discharges [2,4]. Current physicochemical approaches for aquatic BrO₃[−] elimination, involving adsorption, separation, chemical reduction, and photo-/electro-catalysis, exhibit limited application potential due to their disadvantages in terms of high energy consumption, stringent optional conditions, and requirements of post-treatment steps [5–7]. Comparably, autotrophic microbial reduction has received increasing interest in the past decade, owing to its proven capacity of cost-efficiently converting BrO₃[−] to innocuous Br[−] under mild circumstances and the organic-deficient nature of most drinking water sources [6,8].

Nitrate (NO₃[−]) is a pervasive contaminant which coexists with BrO₃[−] at a typical concentration range of 10–30 mg N/L in surface water and groundwater, and which can

result in methemoglobinemia in infants [8–11]. This accentuates the necessity to develop robust technology capable of simultaneously eliminating BrO_3^- and NO_3^- from polluted drinking water sources. As an advanced autotrophic microbial reduction technology, the H_2 -based membrane biofilm reactor (H_2 -MBfR) has been successfully practiced at a pilot and/or commercial scale for eradicating a variety of oxidized pollutants, e.g., BrO_3^- , NO_3^- , sulfate, perchlorate, selenate, and chromate [9,12]. In this system, electron donor H_2 diffuses through the wall of gas-permeable hollow fiber membranes (HFM), and supports the functional microorganisms in the HFM-attached biofilm to respire the electron acceptors (i.e., oxidized pollutants); such a scheme of passive gas delivery enables the full utilization of H_2 , as well as the efficient removal of targeted contaminants [9,13]. Several case studies have shown that, when the influent concentrations of BrO_3^- and NO_3^- were in the range of 0.1–1.5 mg/L and 5–20 mg N/L, respectively, which were approachable to those in real drinking water sources, the appreciable removal (beyond 95%) of both oxyanions could be realized in H_2 -MBfRs [1,8].

In H_2 -MBfRs, the biofilm microorganisms, which can dominate the reduction of BrO_3^- and NO_3^- , are defined as bromate-reducing bacteria (BRB) and denitrifying bacteria (DNB), respectively [1,11]. Since H_2 is shared by functional bacteria (e.g., BRB and DNB) in the biofilm as the sole electron donor to drive the reduction of oxidized pollutants, the microbial competition for H_2 availability (controlled by H_2 supplying pressure) inevitably occurs in H_2 -MBfRs [14]. The results of empirical studies corroborated that BrO_3^- and NO_3^- concentrations were critical to the efficiencies of microbial reduction, and the BrO_3^- reduction processes could be inhibited in the case of exorbitant NO_3^- loading [11,15]. Microbial community investigations have revealed the variation trends in the species and abundance of BRB and DNB in the biofilm systems under diverse BrO_3^- and NO_3^- loadings [6,11]. Despite the above progress, it remains understudied the extent to which the critical operating parameters drive the evolution of biofilm microenvironment, structure, and activity of the H_2 -MBfR for simultaneous BrO_3^- and NO_3^- elimination. This constitutes a major hindrance to our understanding of the interaction mechanism between BRB and DNB in the biofilm. The development of a systematic and quantitative framework might be a solution to this concern, given the difficulty in the use of present experimental means for elucidating the stratification features of biofilm.

The one-dimensional, multispecies biofilm model, developed on the AQUASIM platform, is a versatile tool applicable to quantitatively assess the steady-state characteristics of the biofilm, e.g., the substrate profiles, as well as microbial distribution and activities [16]. To date, a model framework, which can be implemented to simulate the simultaneous removal processes of BrO_3^- and NO_3^- in the H_2 -MBfR, is still unavailable in the literature. In this work, a sophisticated biofilm model was established on the AQUASIM platform to mechanistically interpret the BrO_3^- and NO_3^- reduction processes of H_2 -MBfR. On the basis of the previous model frameworks for NO_3^- removal [14,16], we proposed an expanded model framework through incorporation into the algorithm for the metabolic process kinetics of BRB, as well as the influences of CO_2 addition (as carbon source and pH regulator) on metabolic process kinetics of BRB and DNB. Long- and short-term experimental data regarding BrO_3^- and NO_3^- removal, obtained from a lab-scale H_2 -MBfR, were used for the calibration of key model parameters and the validation of the model outputs, respectively. The validated model was then applied to evaluate the gradients of substrates (H_2 , BrO_3^- , and NO_3^-), as well as the distribution and activities of BRB and DNB in the biofilm, in the case of changing system operating parameters including the H_2 pressure, CO_2 addition, and influent BrO_3^- and NO_3^- concentrations.

2. Materials and Methods

2.1. Reactor Setup and Start-Up

The schematic of the H_2 -MBfR used in this study is shown in Figure 1. The reactor consisted of a module containing 96 HFMs (Litree Company, Suzhou, China) and a microporous tube placed in a plexiglass cylinder (height = 22 cm, inner diameter = 6 cm,

effective volume = 0.56 L). The average outer diameter and pore size of HFM was 1.5 mm and 0.02 μm , respectively, and the total membrane surface area of HFM module was 633 cm^2 . The module with a sealed lower end was connected to a H_2 tank for delivering pressurized H_2 . Pure CO_2 was supplied by the microporous tube with its bottom end linked to a CO_2 tank to serve as carbon source and pH regulator. Synthetic influent was introduced into the reactor via a peristaltic pump (BT101L-DG-1, Lead Fluid, Baoding, China), and the effluent was collected from the outlet of the reactor. A recirculation pump (BT101L-YZ15/25, Lead Fluid, Baoding, China) was sustained at a high flowrate of 100 mL/min to keep the bulk liquid completely mixed. The reactor was inoculated with 50 mL of biomass collected from a denitrifying H_2 -MBfR in our lab. The synthetic influent, containing 10 mg N/L NaNO_3 with an identical composition to that described in Li et al. [17], was used in the start-up period of the reactor. During the start-up period, the influent flowrate was maintained at 1.6 mL/min (resulting in an HRT of 5.8 h), and the H_2 and CO_2 pressure was kept at 0.04 and 0.012 MPa, respectively. After 30 days of operation, the influent flowrate was changed to 2.0 mL/min (corresponding to an HRT of 4.7 h) until the biofilm was well formed, and the performance of the reactor reached a steady state with stable NO_3^- removal.

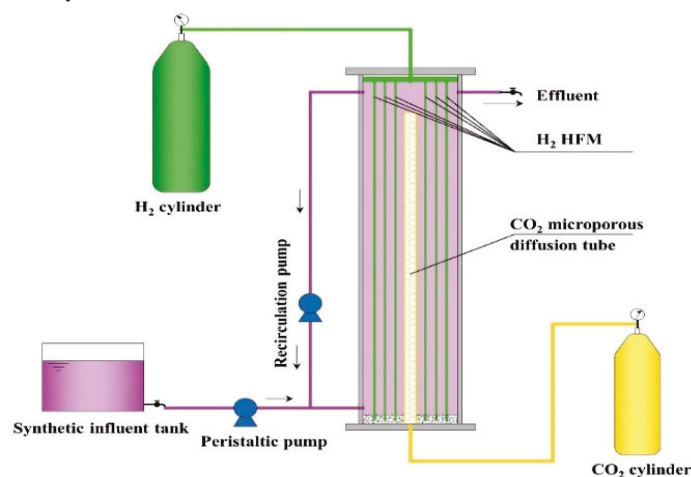


Figure 1. Schematic of the H_2 -MBfR.

2.2. Short- and Long-Term Experiments and Sample Analysis

On days 31–40 of stage 1, short-term experiments were performed to assess the effects of H_2 pressure (0.01–0.08 MPa), influent NO_3^- (1–20 mg N/L), and CO_2 pressure (0.004–0.036 MPa) on the NO_3^- and BrO_3^- removal of the H_2 -MBfR. The detailed information concerning the operational conditions of short-term experiments can be found in Table S1. For each experiment, one system operating parameter was changed, while keeping the others fixed. Once the experiment condition was changed, aqueous samples were collected after three HRT operations of the system, in order to allow the stabilization of effluent contaminant concentrations [18]. Following the short-term experiments, long-term experiments (days 41–140) were carried out to investigate how the oxyanion removal performance of the system responded to the changing BrO_3^- loadings. As summarized in Table S2, in long-term experiments, the influent concentrations of BrO_3^- were set at 0.1, 0.5, and 1.0 mg/L in stage 3, stage 4, and stage 5, respectively, and the H_2 and CO_2 pressure were maintained at 0.04 and 0.012 MPa, respectively.

The collected aqueous samples were filtered immediately through a 0.22 μm pore size polycarbonate membrane filter (Anpel Co., Ltd., Shanghai, China) and stocked in a refrigerator (4 $^\circ\text{C}$) until analyzed. The concentrations of NO_3^- , NO_2^- , and BrO_3^- were determined by ion chromatography (ICS-1000, Dionex, Sunnyvale, USA) equipped with an AS-19 column (4 $\times$ 250 mm, Dionex, Sunnyvale, USA). The dissolved H_2 was determined using a H_2 microsensor (H_2 10, Unisense A/S Corp., Aarhus, Denmark). The pH value was

measured using a pH meter (pHS-3C model, Leici, Shanghai, China). The contaminant removal flux was calculated using Equation (1):

$$J = \frac{Q}{A}(S_i - S_e), \quad (1)$$

where J is the NO_3^- and BrO_3^- removal flux in units of $\text{g N}/(\text{m}^2 \cdot \text{day})$ and $\text{g BrO}_3^-/(\text{m}^2 \cdot \text{day})$, respectively, Q signifies the influent flowrate (m^3/day), A refers to the total membrane surface area (m^2), and S_i and S_e denote the influent concentration of NO_3^- or BrO_3^- and the effluent concentration of NO_3^- or BrO_3^- , respectively.

2.3. Model Development and Evaluation

2.3.1. Model Framework Development

Unlike the classical biofilm models established by Tang et al. [14,16], the framework of the developed mathematical model involves the biochemical process of hydrogenotrophic BrO_3^- reduction, and it considers the effects on the metabolic process kinetics of BRB and DNB in the case of CO_2 addition (as carbon source and pH regulator). Figure 2 shows the schematic of the involved biochemical processes and the correlated interactions between the model components in the biofilm. The model components include five solid components (i.e., BRB, DNB, heterotrophic bacteria (HB), extracellular polymeric substances (EPS), and inert organics (IO)) and five dissolved components (i.e., H_2 , CO_2 , NO_3^- , BrO_3^- , and soluble microbial products (SMP)). H_2 is exploited by BRB and DNB as the electron donors, BrO_3^- and NO_3^- as the electron acceptors, and CO_2 as the carbon source. In the conversion processes of BrO_3^- and NO_3^- to Br^- and N_2 , BRB and DNB obtain energy to sustain their growth and metabolism. H_2 was the sole energy source of the hydrogenotrophic bacteria, since no organic carbon was introduced to the influent; thus, BRB and DNB could merely abstract electrons from H_2 to drive the BrO_3^- and NO_3^- reduction. HB grows either on the SMP directly produced by BRB and DNB or indirectly on the hydrolyzed EPS (i.e., SMP) originated from BRB and DNB. The decay of BRB, DNB, and HB generates nonbiodegradable IO. The electrons provided from H_2 can be classified into three portions during the BRB and DNB metabolic processes: bacterial cell synthesis (k_1), SMP formation (k_2), and EPS formation (k_3); thus, $k_1 + k_2 + k_3 = 1$. The electrons for cell synthesis are subdivided into the fraction for energy-providing reaction (f_e^0) and the other for synthesis reaction of true yield of biomass (f_s^0); therefore, $f_e^0 + f_s^0 = 1$. Here, f_d represents the fraction of biodegradable biomass; hence, $1 - f_d$ refers to the remaining nonbiodegradable biomass.

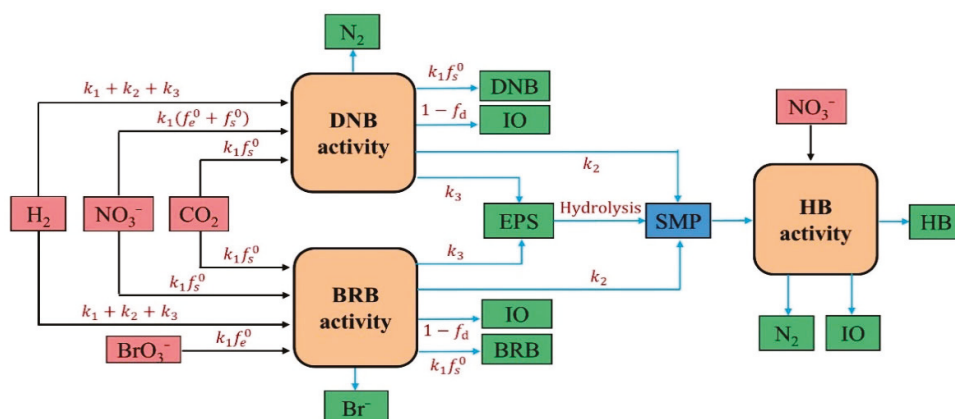


Figure 2. Schematic of the interactions between model components involved in the biochemical processes of the biofilm.

2.3.2. Model Solution and Calibration

The numerical solution of the model was implemented on software AQUASIM 2.1g, by inputting the process matrix (Table 1), stoichiometric and kinetic parameters (Table S3), process kinetic rate equations (Table 2), and experiment operational parameters of the

H₂-MBfR (Table S4). In particular, the calculation procedure for stoichiometric coefficients of model components (shown in Table 1) in the BRB metabolic process is exhibited in Section S1. Table S3 merely lists the calculated and recalibrated stoichiometric and kinetic parameters of the BRB metabolic process in this work, while other pertinent parameters can be found in Table S5. Bulk liquid pH is known to be a key factor correlated to the activities of the hydrogenotrophic microorganisms [13,19,20]. In order to quantitatively assess how bulk liquid pH affects the microbial metabolic activities, the inhibition factor of bulk liquid pH (f_{pH}) was introduced to the kinetic rate expressions of the model framework, as shown in Table 2. According to the normalized Michaelis pH function [21], f_{pH} can be computed using Equation (2).

$$f_{pH} = \frac{1 + 2 \cdot 10^{0.5(pK_l - pK_h)}}{1 + 10^{(pH - pK_h)} + 10^{(pK_l - pH)}} \quad (2)$$

where pH values are the experimental measurements in this study; pK_h and pK_l denote the upper and lower pH values at which the metabolic rates are equal to 50% of the maximum rate at the optimum pH, respectively, and their values of 9.04 and 6.27 were adopted from previous studies [21–23].

Table 1. Process matrix for the developed model of components.

Component (i) Process (j)	S _{H2}	S _{NO3}	S _{BrO3}	S _{SMP}	S _{CO2}	X _{DNB}	X _{BRB}	X _{HB}	X _{IO}	X _{EPS}
DNB growth	$-\frac{14}{5f_{s,DNB}^0}$	$-k_1 \left(\frac{28f_{e,DNB}^0}{25f_{s,DNB}^0} + \frac{1}{5} \right)$		k_2	$-k_1$	k_1				k_3
BRB growth	$-\frac{14}{5f_{s,BRB}^0}$	$-\frac{1}{5}k_1$	$-k_1 \frac{14f_{e,DNB}^0}{15f_{s,DNB}^0}$	k_2	$-k_1$		k_1			k_3
HB growth		$-\frac{1-Y_{HB}}{1.25Y_{HB}}$		$-\frac{1}{Y_{HB}}$				1		
DNB decay						-1			$1-f_d$	
BRB decay							-1		$1-f_d$	
HB Decay								-1	$1-f_d$	
Hydrolysis				1						-1
	H ₂ (mol/m ³)	NO ₃ (mol/m ³)	BrO ₃ (mol/m ³)	SMP (mol/m ³)	CO ₂ (mol/m ³)	DNB (mol/m ³)	BRB (mol/m ³)	HB (mol/m ³)	IO (mol/m ³)	EPS (mol/m ³)

Table 2. Process kinetic rate equations for the developed model.

Process (j)	Kinetic Rate Expressions
DNB growth	$\mu_{DNB} \frac{S_{H2}}{S_{H2} + K_{H2}^{DNB}} \frac{S_{NO3}}{S_{NO3} + K_{NO3}^{DNB}} \frac{S_{CO2}}{S_{CO2} + K_{CO2}^{DNB}} X_{DNB} f_{pH}$
BRB growth	$\mu_{BRB} \frac{S_{H2}}{S_{H2} + K_{H2}^{BRB}} \frac{S_{NO3}}{S_{NO3} + K_{NO3}^{BRB}} \frac{S_{BrO3}}{S_{BrO3} + K_{BrO3}^{BRB}} \frac{S_{CO2}}{S_{CO2} + K_{CO2}^{BRB}} X_{BRB} f_{pH}$
HB growth	$\mu_{HB} \frac{S_{NO3}}{S_{NO3} + K_{NO3}^{HB}} \frac{S_{SMP}}{S_{SMP} + K_{SMP}^{HB}} X_{HB} f_{pH}$
DNB decay	$b_{DNB} X_{DNB}$
BRB decay	$b_{BRB} X_{BRB}$
HB Decay	$b_{HB} X_{HB}$
Hydrolysis	$k_{hyd} X_{EPS}$

Disparate reactor configurations, operating conditions, and HFM patterns commonly result in the varying compositions and metabolic kinetics of biofilms [24]. For the aim of matching the specific simulation scenarios, several parameters, i.e., H₂ transfer coefficient of HFM (K_m), maximum specific growth rate of DNB and BRB (μ_{DNB} and μ_{BRB}), and half-maximum-rate concentration of BrO₃[−] for BRB (K_{BrO3}), were recalibrated by fitting the measured effluent NO₃[−] and BrO₃[−] concentrations of the long-term operated system to the modeled results using the AQUASIM built-in iterative algorithms (Equation (3)).

By minimizing the square error sums between the model predictions and experimental measurements, the selected parameters were calibrated to be the best-fit values.

$$\chi^2(p) = \sum_{i=1}^n \left(\frac{y_{\text{meas},i} - y_i(p)}{\sigma_{\text{meas},i}} \right)^2, \quad (3)$$

where $y_{\text{meas},i}$ and $y_i(p)$ represent the experimental results and model predictions at time i , and $\sigma_{\text{meas},i}$ and n signify the standard deviation and number of data points, respectively.

2.3.3. Model Validation and Evaluation

The calibrated model was further validated by comparing the simulated results with experimentally measured NO_3^- and BrO_3^- removal fluxes in the short-term experiments. The validated model was then used to simulate the profiles of substrates, microbial distribution, and metabolic activities in the biofilm of the H_2 -MBfR operated in a series of system conditions, including influent BrO_3^- concentrations (0.1–1.0 mg/L), H_2 pressure (0.01–0.08 MPa), influent NO_3^- concentration (1–20 mg N/L), and CO_2 pressure (0.004–0.036 MPa), in order to investigate the evolution laws of biofilm microenvironment, structure, and activity in the H_2 -MBfR for NO_3^- and BrO_3^- removal, in the case of changing system conditions. A schematic of the research methodology is shown in Figure 3.

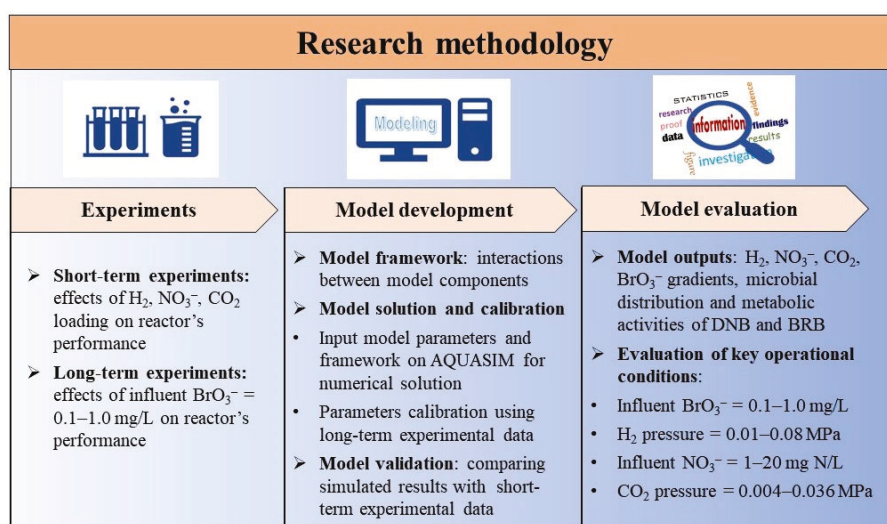


Figure 3. Schematic of the research methodology.

3. Results and Discussion

3.1. Long-Term H_2 -MBfR Performance and Model Calibration

The long-term experimental data obtained during the 140 days of operation of H_2 -MBfR were used for the recalibration of the selected parameters by fitting the effluent NO_3^- and BrO_3^- concentrations to those of simulated results. As shown in Figure 4, the measured data and simulated results were finely matched with the corresponding coefficients of determination (R^2) up to 0.93 and 0.91 for the effluent NO_3^- and BrO_3^- concentrations, respectively. The analysis results concerning the sensitivity of the selected parameters to the effluent BrO_3^- and NO_3^- concentrations in the long-term operated H_2 -MBfR are shown in Figure 5. It can be found that the effluent BrO_3^- concentration of the H_2 -MBfR was most sensitive to μ_{BRB} and relatively sensitive to μ_{DNB} and K_m (Figure 5a), while the effluent NO_3^- concentration was sensitive to K_m and μ_{DNB} (Figure 5b). These results are in line with the findings of previous studies, i.e., the maximum specific growth rate of microorganisms and the H_2 transfer coefficient of HFM were sensitive to the H_2 -MBfR performance [9,24,25]. The best-fit values of K_m , μ_{BRB} , μ_{DNB} , and K_{BrO_3} were estimated to be 0.189 m/day, 0.85 day^{−1}, 0.57 day^{−1}, and 0.014 mg/L, respectively.

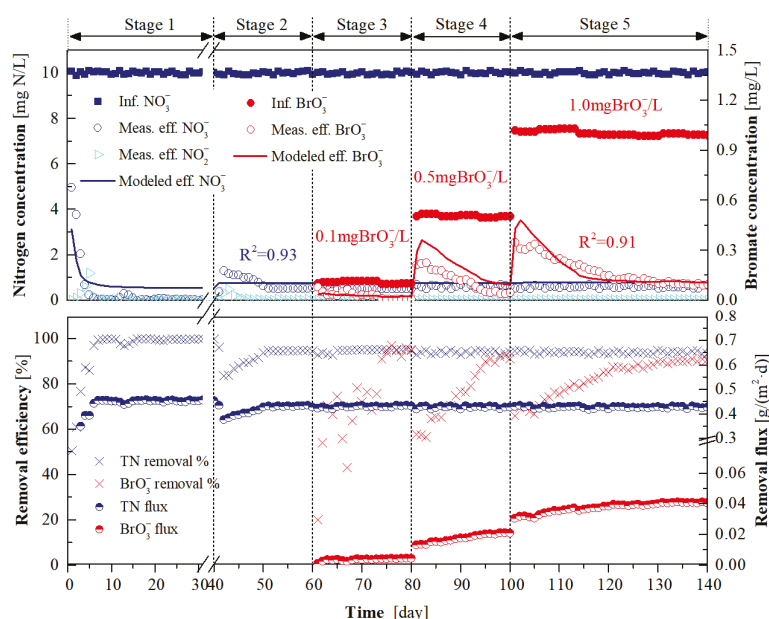


Figure 4. Long-term performance of NO_3^- and BrO_3^- reduction in the H_2 -MBfR. The abbreviations “Inf.”, “Eff.”, and “Meas.” denote influent, effluent, and measured, respectively.

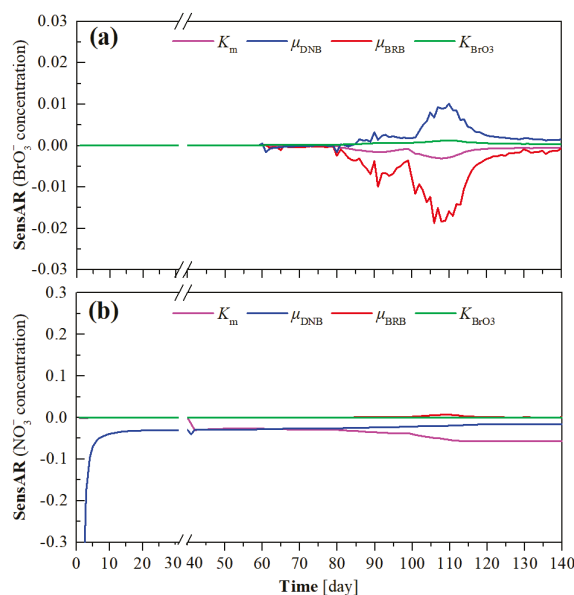


Figure 5. Sensitivities of the effluent BrO_3^- (a) and NO_3^- (b) concentrations to the selected parameters K_m , μ_{DNB} , μ_{BRB} , and K_{BrO_3} .

It can be also seen from Figure 4 that, after 7 days of start-up at stage 1, the denitrification flux of the H_2 -MBfR stabilized at around $0.45 \text{ g N}/(\text{m}^2 \cdot \text{day})$, corresponding to a NO_3^- removal efficiency of over 99%. The slightly decreased denitrification flux of the system at stage 2 can be ascribed to the augment in the influent flowrate from $1.6 \text{ mL}/\text{min}$ at stage 1 to $2.0 \text{ mL}/\text{min}$ at this stage. The introduction of 0.1 – $1.0 \text{ mg}/\text{L}$ BrO_3^- into the influent at stages 3–5 did not further decrease the denitrification performance of the system, given the identical average denitrification flux ($0.42 \text{ g N}/(\text{m}^2 \cdot \text{day})$) at days 50–60 of stage 2 (without BrO_3^- addition) and stages 3–5. This observation is in agreement with the results of previous studies that a BrO_3^- concentration below $50 \text{ mg}/\text{L}$ had no inhibitory effect on denitrification [15,26]. Empirical studies suggest that it usually takes 11–40 days to enable the H_2 -MBfRs to reach steady-state characteristics following the adjustment of operation conditions such as substrate loadings and HRT [17,27]. Similarly, our results

indicate that, in the case of BrO_3^- addition, it took 15–25 days at stages 3–5 to enable the BrO_3^- removal of the H_2 -MBfR to reach a steady state. The stabilized BrO_3^- removal flux was increased from $0.0044 \text{ g}/(\text{m}^2 \cdot \text{day})$ at stage 3 to $0.041 \text{ g}/(\text{m}^2 \cdot \text{day})$ at stage 5. This is presumably attributed to the augment in the abundance and/or reduction rate of BRB with increasing influent BrO_3^- concentration. Furthermore, Downing and Nerenberg [15] found that a near 11-fold increase in the BrO_3^- removal flux of H_2 -MBfR was achieved when the influent BrO_3^- concentration was increased from 0.1 to 10 mg/L.

3.2. Short-Term H_2 -MBfR Performance and Model Validation

Short-term experiments were performed to evaluate the effects of the key influencing factors, i.e., H_2 pressure, influent NO_3^- concentration, and CO_2 pressure, on the NO_3^- and BrO_3^- reduction of the H_2 -MBfR. As shown in Figure 6a,b the determined BrO_3^- and NO_3^- removal fluxes were increased from 0.036 and 0.36 to $0.041 \text{ g}/(\text{m}^2 \cdot \text{day})$ and $0.42 \text{ g N}/(\text{m}^2 \cdot \text{day})$, respectively, as the H_2 pressure was increased from 0.01 to 0.04 MPa. This is likely owing to the increased availability of electron donor, which enhanced the activities of BRB and DNB. A higher H_2 pressure (0.06 and 0.08 MPa) did not ameliorate the BrO_3^- and NO_3^- removal, but led to the consumption of the remaining H_2 in the effluent. Figure 6c,d delineate that, although the BrO_3^- and NO_3^- were all accumulated in the effluent, the NO_3^- removal flux was increased from 0.42 to $0.51 \text{ g N}/(\text{m}^2 \cdot \text{day})$, accompanied by the significant decrease in BrO_3^- removal flux from 0.041 to $0.011 \text{ g}/(\text{m}^2 \cdot \text{day})$, when the influent NO_3^- concentrations were augmented from 10 to 20 mg N/L. In accordance with this, Zhong et al. [6] observed that an influent NO_3^- concentration of 11.3 mg N/L was able to inhibit the BrO_3^- reduction in the H_2 -MBfR, which gave rise to the advantage of DNB over BRB when competing for electron donors. CO_2 is arguably one of the most effective pH regulators in H_2 -MBfRs, and it can serve as the supplemental inorganic carbon source for hydrogenotrophic bacteria [13,28]. As depicted in Figure 6e,f, the shift of CO_2 pressure from 0.012 to 0.036 MPa led to an apparent decline in the NO_3^- removal flux from $0.42 \text{ g N}/(\text{m}^2 \cdot \text{day})$ at 0.012 MPa to $0.32 \text{ g N}/(\text{m}^2 \cdot \text{day})$ at 0.036 MPa, but had a negligible influence on BrO_3^- removal flux. A plausible explanation is that, as the CO_2 pressure was in the range of 0.020–0.036 MPa, the resultant bulk liquid pH of 6.0–6.9 was obviously lower than the reported favorable pH range (7.0–9.0) of DNB, according to existing studies [19,20], and some specific BRB was possibly able to endure more acidic conditions. Additionally, the measured removal fluxes of BrO_3^- and NO_3^- in the short-term experiments were employed to further validate the calibrated model. It can be observed from Figure 6b–f that, in all cases, the modeled results were quite approximate to the experimental data, indicating the good accuracy and reliability of the developed model for prediction of the simultaneous BrO_3^- and NO_3^- reduction processes in the H_2 -MBfR.

3.3. Model Evaluation of the Effects of BrO_3^- Loading

Figure 7 shows the simulated distribution of substrates, DNB and BRB fractions, as well as their metabolic activities, in the steady-state biofilms at stages 3–5 using the validated model. As shown in Figure 7a–c, in line with the counter-diffusional characteristics of dissolved substrate in H_2 -MBfR biofilm [29], the H_2 concentration gradually decreased from HFM surface (i.e., biofilm thickness of zero point) toward to the bulk liquid side, while the other substrates (including CO_2 , NO_3^- , and BrO_3^-) originated from bulk liquid presented the contrary tendency. H_2 and CO_2 concentrations across the biofilm exhibited negligible difference when the influent concentration varied in the range of 0.1–1.0 mg/L (Figure 7a), attributed to the limited electron donor and carbon source consumption by BRB at low BrO_3^- loadings. It can also be seen from Figure 7a that CO_2 was not a limiting factor as a carbon source for BRB and DNB anabolism, since its concentrations within the whole biofilm were much higher than the half-maximum-rate concentration (0.004 mg/L) adopted in the model. Moreover, the resultant bulk liquid pH 7.5 at the CO_2 pressure of 0.012 MPa would not adversely affect the metabolic processes of BRB and DNB, since the maximum NO_3^- and BrO_3^- removal fluxes were attained at this CO_2 pressure, as shown

in Figure 6f. In line with this, the optimal pH reported for hydrogenotrophic denitrification and bromate reduction has been documented at neutral or weakly alkaline values [13,15].

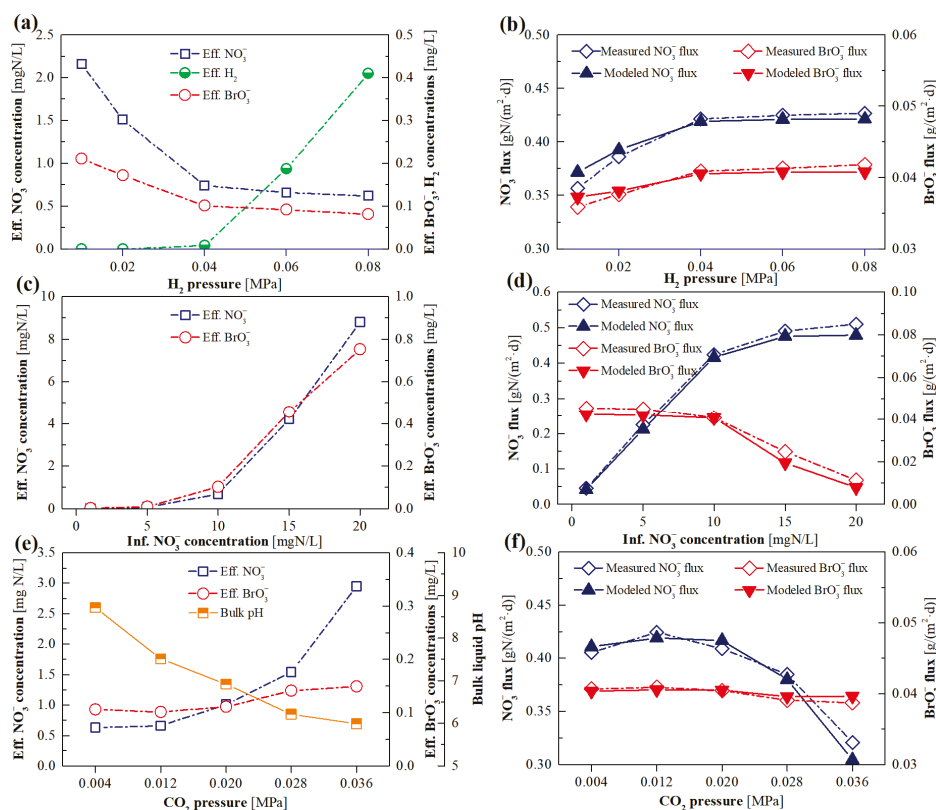


Figure 6. The system performance of the H₂-MBfR, as well as the comparison of the measured and simulated removal fluxes of NO₃⁻ and BrO₃⁻, in the case of changing H₂ pressure (a,b), influent NO₃⁻ concentration (c,d), and CO₂ pressure (e,f).

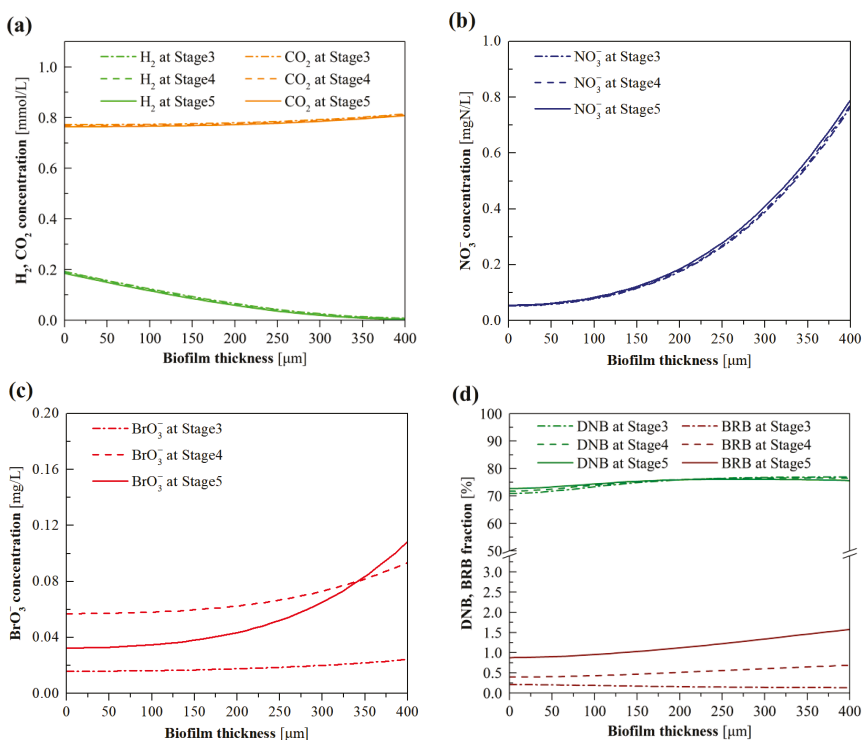


Figure 7. Cont.

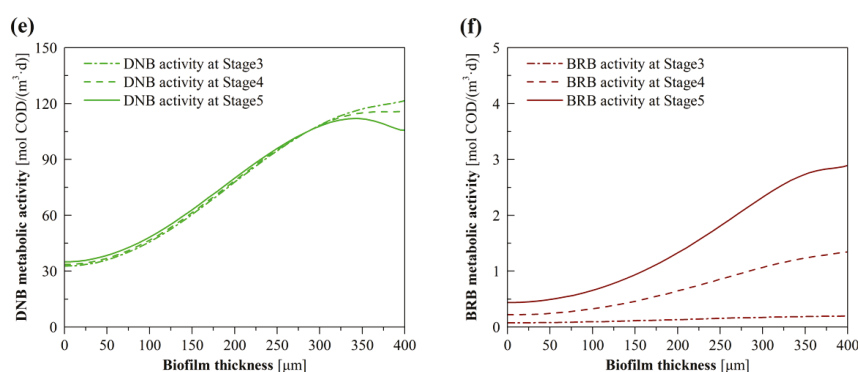


Figure 7. Model-simulated profiles for (a) H_2 and CO_2 , (b) NO_3^- , (c) BrO_3^- concentrations, and (d) DNB and BRB fractions, as well as (e) DNB and (f) BRB metabolic activities, in the biofilm of H_2 -MBfR as a function of influent BrO_3^- concentration ranging from 0.1 to 1.0 mg/L.

Figure 7d plots the simulated profiles of DNB and BRB fractions in the biofilm. DNB dominated in the biofilm compared to BRB at all stages, indicating that DNB outcompeted BRB for space, likely associated with the much higher concentration of NO_3^- in the biofilm than BrO_3^- . In particular, in response to the increase of the influent BrO_3^- concentration from stage 3 to stage 5, the BRB fraction (proportion) obviously increased in the biofilm. Figure 7e shows the DNB activity in the biofilm as a function of influent BrO_3^- concentration. The declined DNB activity in the biofilm range of 0–210 μm was mainly due to the inhibition of electron acceptors for DNB metabolism, given that the NO_3^- concentrations within this range were below the half-maximum-rate concentration of NO_3^- for DNB (0.2 mg N/L) [14]. The observed decrease in DNB activity from stage 3 to stage 5 at the outer layer biofilm was the result of the lower H_2 concentrations. As shown in Figure 7f, the BRB activity in the biofilm increased from stage 3 to stage 5, owing to the augmented BRB fraction and BrO_3^- gradients in the biofilm, which facilitated the metabolism of BRB. In addition, the increased BRB fraction and activity, as exhibited in Figure 7d,f, helps explain the augmented BrO_3^- removal flux from stage 3 to stage 5 (Figure 4).

3.4. Model Evaluation of the Effects of H_2 Pressure

Empirical studies [13,20] have collectively shown that excessive H_2 supply pressure results in the H_2 off-gassing problem, while an insufficient supply leads to unsatisfactory pollutant removal due to the electron donor scarcity in biofilms. Figure 8a plots the simulated H_2 and CO_2 concentration profiles in the biofilm at diverse H_2 pressure (0.01–0.08 MPa). The H_2 concentration in the biofilm increased with the increase in H_2 pressure. At the H_2 pressure of 0.01 MPa, more than half of the outer biofilm region (biofilm thickness > 200 μm) could not deliver sufficient H_2 . H_2 constitutes a limiting factor for microbial metabolic processes when its content is below the half-maximum-rate concentration. When H_2 pressure was increased to 0.04 MPa, the H_2 contents across the biofilm were all higher than the half-maximum-rate concentrations of H_2 for DNB and BRB metabolism (0.002 mg/L) [14]; thus, it can be inferred that the H_2 concentration within biofilm was not a decisive factor limiting NO_3^- and BrO_3^- removal at relatively high H_2 pressure. Note that, at this H_2 pressure, the simulated H_2 concentration in the bulk liquid was 0.0074 mg/L, which is quite close to the measured result (0.008 mg/L) during the short-term experiments (Figure 6a) and is also comparable to the recommended aquatic H_2 concentration (0.009 mg/L) in H_2 -MBfR [18]. Upon further increasing the H_2 pressure, the H_2 off-gassing phenomenon occurred. It can also be seen from Figure 8a that the CO_2 concentration gradients in the biofilm hardly changed when the H_2 pressure was higher than 0.04 MPa. This implies that the excessive H_2 supply would not accelerate the carbon source utilization of BRB and DNB.

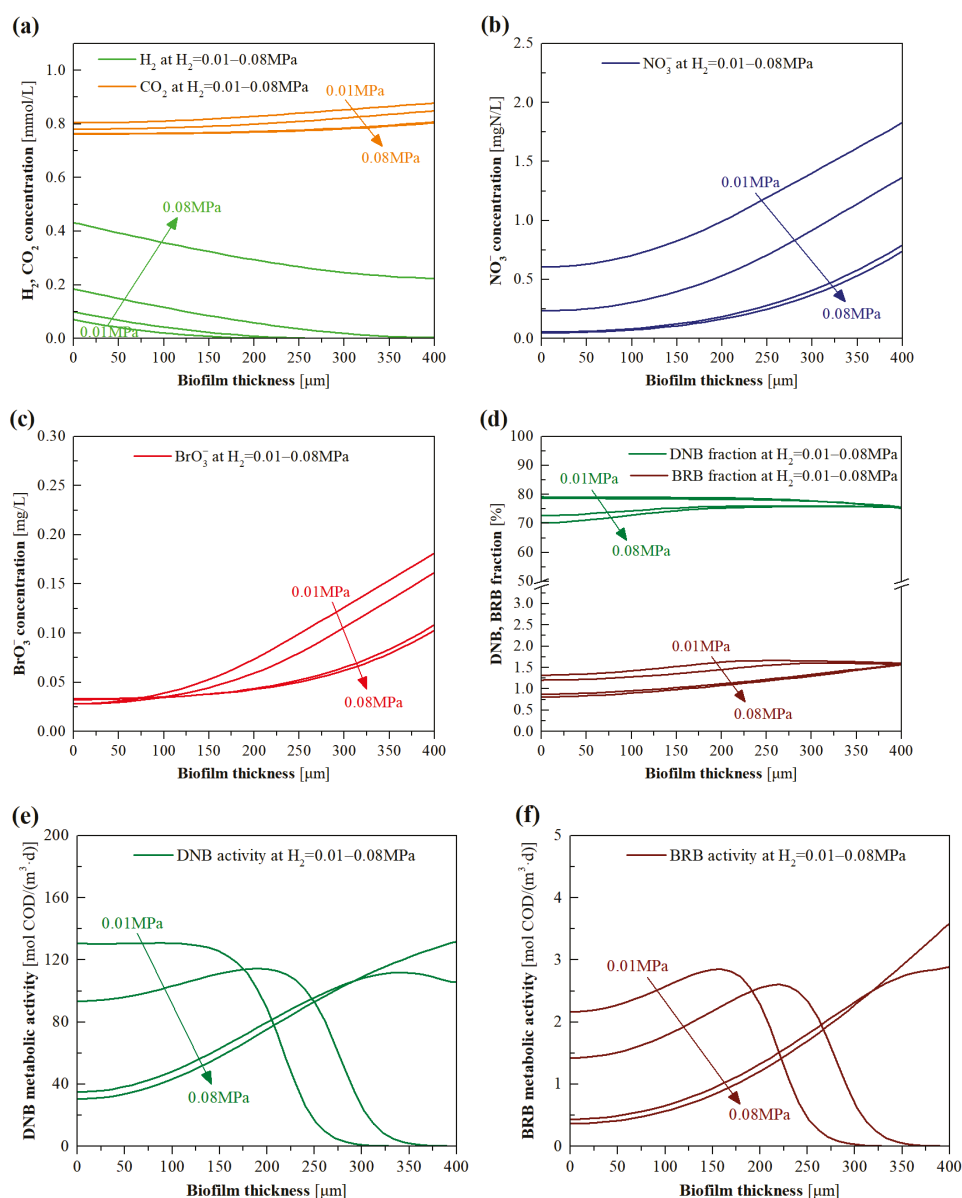


Figure 8. Model simulated profiles for (a) H₂ and CO₂, (b) NO₃⁻, (c) BrO₃⁻ concentrations, and (d) DNB and BRB fractions, as well as (e) DNB and (f) BRB metabolic activities, in the biofilm of H₂-MBfR as a function of H₂ pressure ranging from 0.01 to 0.08 MPa.

As depicted in Figure 8b,c, with the increase in H₂ pressure from 0.01 to 0.04 MPa, the NO₃⁻ and BrO₃⁻ concentrations in the biofilm were found to markedly decline. This can be explained by the increased H₂ availability for DNB and BRB compared to the biofilm exterior, which allowed a greater reduction in NO₃⁻ and BrO₃⁻ in the exterior rather than the interior of biofilm. However, NO₃⁻ and BrO₃⁻ concentration gradients hardly varied once the H₂ pressure exceeded 0.04 MPa, which is in accordance with the experimental findings of the short-term experiments that the NO₃⁻ and BrO₃⁻ removal marginally changed at the excessive H₂ pressure (shown in Figure 6b). According to the simulated BrO₃⁻ concentration profiles, BrO₃⁻ concentrations in the biofilm were all greater than its calibrated half-maximum-rate concentration (0.014 mg/L) at the simulated H₂ pressure range, indicating that BrO₃⁻ loading was also not a limiting factor to BRB activity. The increased H₂ availability in the outer layer of the biofilm resulted in the extension of the active region of DNB and BRB from the biofilm interior to the whole biofilm, as revealed in Figure 8e,f. In particular, the decreased activities of DNB and BRB in the inner layer of biofilm with increasing H₂ pressure were mainly the consequence of the concurrently

decreased concentrations of NO_3^- and BrO_3^- (Figure 8b,c) and the fractions of DNB and BRB (Figure 8d). In the case of low H_2 pressure (0.01 and 0.02 MPa), the biofilm thicknesses of 200 and 260 μm were the locations where the H_2 concentrations were all below the half-maximum-rate concentrations of DNB and BRB (Figure 8a); beyond these thicknesses, the metabolic activities of DNB and BRB began to dramatically decrease, as delineated in Figure 8e,f.

3.5. Model Evaluation of the Effects of NO_3^- Loading

The experimental results, as shown in Figure 6c, corroborate that the NO_3^- loading significantly impacted the BrO_3^- removal of the H_2 -MBfR. To understand the underlying mechanism, we employed the validated model to simulate the substrate profiles and microbial activities in the biofilm at the influent NO_3^- concentrations of 1–20 mg N/L. As shown in Figure 9a, the H_2 and CO_2 concentration gradients in the biofilm sharply decreased with increasing influent NO_3^- concentration, implying that high NO_3^- loadings might signally enhance the activity of DNB, leading to greater consumption of these two substrates. In particular, H_2 off-gassing was found at the influent NO_3^- concentration lower than 10 mg N/L, owing to the lack of an electron acceptor for H_2 consumption. Once the influent NO_3^- concentration was greater than 10 mg N/L, NO_3^- was found to accumulate in the biofilm with high concentrations (Figure 9b), presumably due to the limitation of overall DNB population, while over 90% of the inputted BrO_3^- could not be consumed by BRB in the biofilm (Figure 9c), suggesting the severe inhibition of BRB activity by high NO_3^- loadings. As exhibited in Figure 9d, when the influent NO_3^- concentration was increased from 1 to 20 mg N/L, the BRB fractions across the biofilm decreased from beyond 20% to approximately 1%, which was accompanied by the surge of the DNB fraction across the biofilm, suggesting the competitive advantage of DNB over BRB in the case of the high NO_3^- loadings.

Figure 9e,f show the simulated DNB and BRB metabolic activities in the biofilm of the system operated under various influent NO_3^- concentrations. As the influent NO_3^- concentration was less than 10 mg N/L, the high DNB and BRB activities appeared at the outer layer of the biofilm, and a closer distance from the HFM side led to lower activities of DNB and BRB. This trend coincides with that of NO_3^- and BrO_3^- concentration gradients in the biofilm, as shown in Figure 9b,c. When the influent NO_3^- concentration was higher than 10 mg N/L, the DNB activities sharply dropped at the biofilm thickness of beyond 210 μm . This is because the H_2 concentrations in the locations beyond this thickness were lower than the half-maximum-rate concentration of DNB (0.002 mg/L). In addition, the BRB activities were strongly inhibited at the higher influent NO_3^- concentration (especially 20 mg N/L), indicating that BRB was overwhelmed by DNB for electron donor competition, when NO_3^- concentration in the influent was much higher than that of BrO_3^- . This is consistent with the previous findings that an excessive influent NO_3^- concentration could inhibit BrO_3^- reduction [6,30].

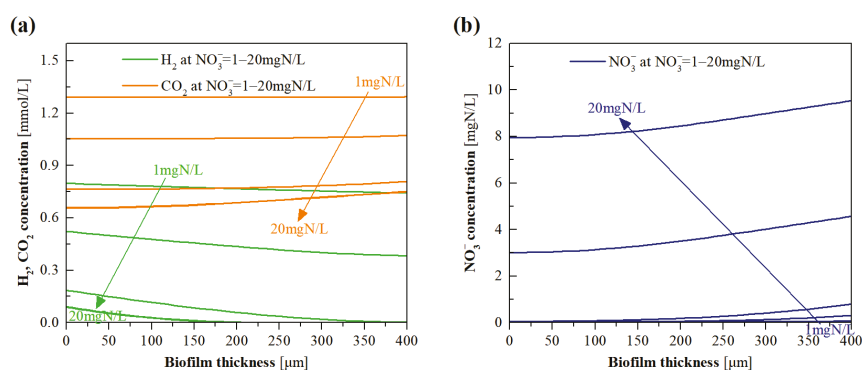


Figure 9. Cont.

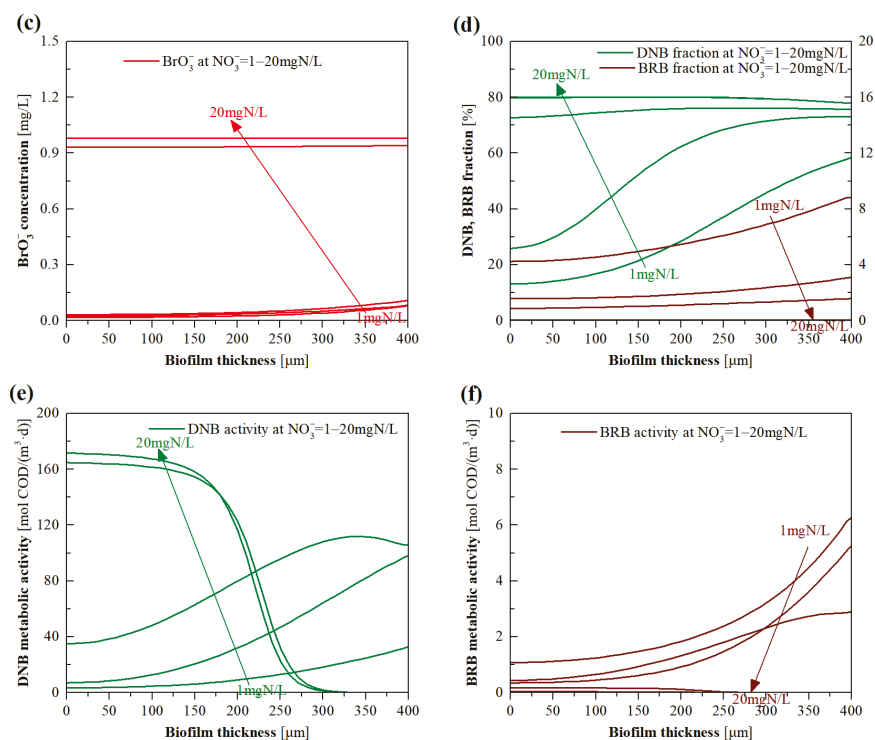


Figure 9. Model simulated profiles for (a) H₂ and CO₂, (b) NO₃⁻, (c) BrO₃⁻ concentrations, and (d) DNB and BRB fractions, as well as (e) DNB and (f) BRB metabolic activities, in the biofilm of H₂-MBfR as a function of influent NO₃⁻ concentration ranging from 1 to 20 mg N/L.

3.6. Model Evaluation of the Effects of CO₂ Pressure

CO₂ has dual functions, i.e., as a carbon source to support microorganism growth and for pH control to regulate the microbial activities in H₂-MBfRs [19,31]. Simulations were, therefore, conducted to investigate the effects of CO₂ addition on the evolution of stratification characteristics of the biofilm at the supply pressure of 0.004–0.036 MPa. As shown in Figure 10a–c, the increase in CO₂ pressure from 0.004 to 0.02 MPa led to insignificant changes in the H₂, NO₃⁻, and BrO₃⁻ concentration gradients of the biofilm. Once the CO₂ pressure was higher than 0.02 MPa, the accumulation of H₂ and NO₃⁻ was increased in the biofilm. The BrO₃⁻ concentrations in the biofilm were slightly increased at the CO₂ pressure of 0.036 MPa. This implies that DNB was more sensitive to the acidic conditions (pH 6.0–6.2 at CO₂ pressure 0.028–0.036 MPa) than BRB.

As depicted in Figure 10d, as the CO₂ pressure was increased from 0.004 to 0.036 MPa, no apparent difference was found in the DNB fractions, while a slight increase in the BRB fractions was observed. It can be seen from Figure 10e,f that, when the CO₂ pressure was less than 0.02 MPa, the DNB and BRB activities in the biofilm all gradually augmented with the increase in distance from the HFM side. This can be attributed to the relatively higher NO₃⁻ and BrO₃⁻ concentrations in the biofilm exterior. It is interesting to note that, compared to the activities of DNB and BRB at the CO₂ pressure below 0.02 MPa, a CO₂ pressure beyond this value gave rise to decreased and increased microbial activities in the exterior and interior of the biofilm, respectively. This can be explained by the fact that DNB and BRB in the biofilm exterior were in the vicinity of the bulk liquid, and the acidification of bulk liquid severely inhibited their metabolic activities; subsequently, the declined activities of microorganisms in the biofilm exterior led to more diffusion of NO₃⁻ and BrO₃⁻ toward the HFM side (Figure 10b,c), which consequently led to increased activities of DNB and BRB in the biofilm interior. When the CO₂ pressure was increased from 0.012 to 0.036 MPa, DNB activity in the majority of the biofilm significantly declined, while the decreased BRB activity in the biofilm exterior was accompanied by an increase in

BRB activity in the biofilm interior (Figure 10e,f). This also indicates that BRB was more tolerant of the acidic aquatic environment than DNB.

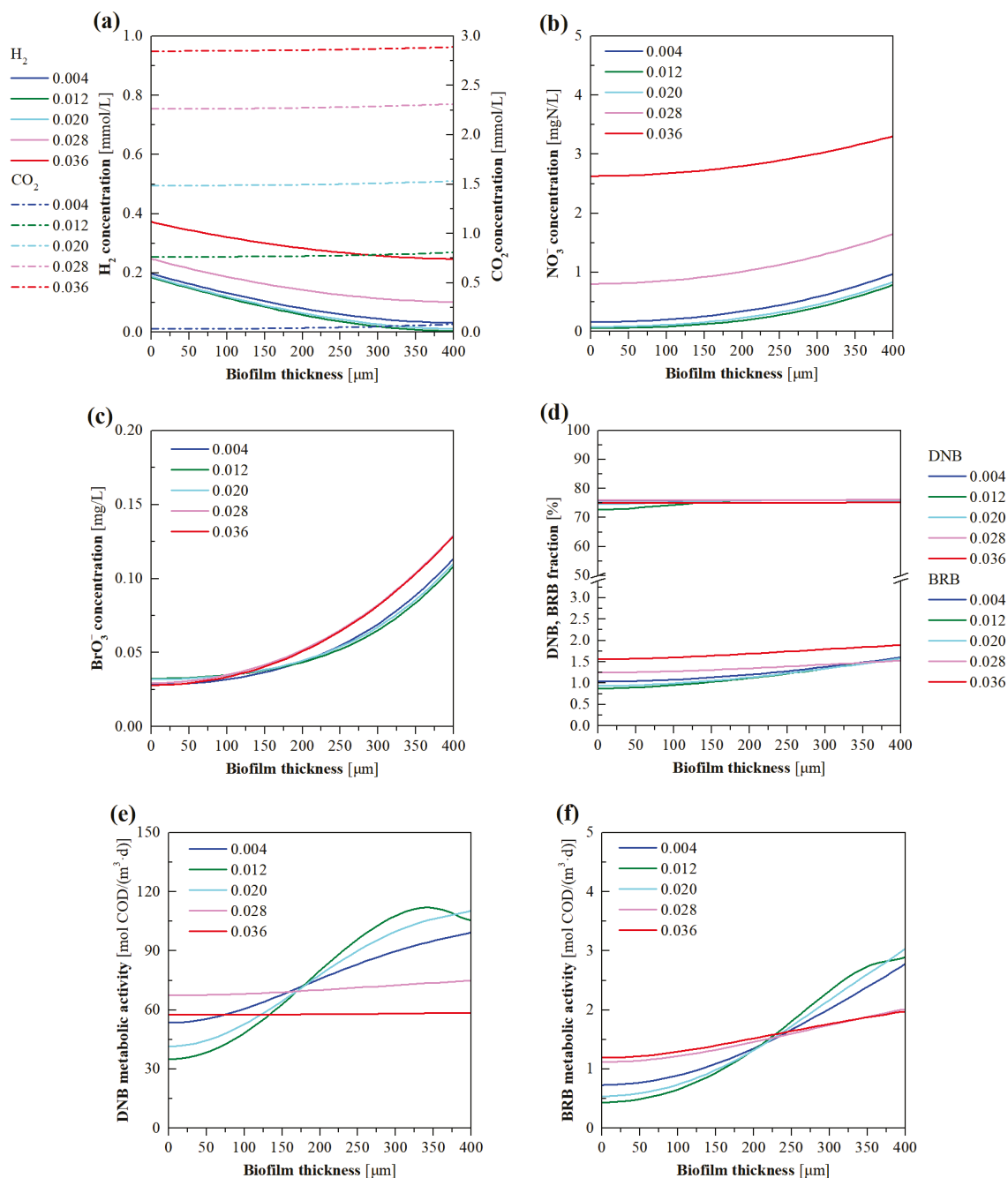


Figure 10. Model simulated profiles for (a) H₂ and CO₂, (b) NO₃⁻, (c) BrO₃⁻ concentrations, and (d) DNB and BRB fractions, as well as (e) DNB and (f) BRB metabolic activities, in the biofilm of H₂-MBfR as a function of CO₂ pressure ranging from 0.004 to 0.036 MPa.

4. Conclusions

An expanded multispecies model was developed to provide key information regarding the microbial BrO₃⁻ and NO₃⁻ reduction processes in the H₂-MBfR in diverse operating conditions. The selected model parameters, K_m , μ_{BRB} , μ_{DNB} , and K_{BrO_3} , were calibrated to the best-fit values of 0.189 m/day, 0.85 day⁻¹, 0.57 day⁻¹, and 0.014 mg/L, respectively. The good agreement between experimental measurements and modeled results indicates the accuracy and reliability of the calibrated model. The evolution of the

substrate gradients, as well as microbial fraction and activity, was driven by the changing system operating parameters involving H_2 pressure, BrO_3^- and NO_3^- loading, and CO_2 pressure. Increasing H_2 pressure led to more efficient BrO_3^- and NO_3^- reduction in the biofilm, but an exorbitant pressure (beyond 0.04 MPa) gave rise to off-gassing of H_2 . The augment in BrO_3^- loading had no significant influence on NO_3^- reduction, while an influent NO_3^- concentration higher than 10 mg N/L resulted in the apparent inhibition of BrO_3^- reduction. A CO_2 pressure over 0.02 MPa had a distinct negative influence on NO_3^- reduction, but minorly impacted BrO_3^- reduction. The simulation results of the developed model offer important mechanistic insights into the BrO_3^- and NO_3^- reduction processes of H_2 -MBfR.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/membranes12080774/s1>: Table S1. Short-term operational conditions of influencing factor experiment of the H_2 -MBfR; Table S2. Start-up and long-term operational conditions of the H_2 -MBfR; Table S3. Stoichiometric and kinetic parameters of BRB related metabolic process for the developed model; Table S4. Experiments operational parameters for the model development; Table S5. Other pertinent input parameters for model development; Section S1. Calculation of the stoichiometric coefficients for BRB metabolic process. Refs. [32,33] are cited on Supplementary Materials.

Author Contributions: Conceptualization, J.Z. (Junjian Zheng), M.J. and H.L.; methodology, M.J. and J.Z. (Junjian Zheng); software, M.J.; validation, Y.Z., J.Z. (Jie Zhang), X.Z. and Z.W.; formal analysis, Y.Z. and X.D.; investigation, Y.Z. and X.D.; resources, J.Z. (Junjian Zheng), H.L., X.Z. and Z.W.; data curation, M.J. and Y.Z.; writing—original draft preparation, M.J.; writing—review and editing, J.Z. (Junjian Zheng); visualization, J.Z. (Junjian Zheng) and J.Z. (Jie Zhang); supervision, X.Z. and Z.W.; project administration, J.Z. (Junjian Zheng); funding acquisition, J.Z. (Junjian Zheng), M.J., Y.Z. and H.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Guangxi Natural Science Foundation (grant number 2022GXNSFFA035033), the National Natural Science Foundation of China (grant numbers 52000046, 52100034, and 51878197), the Special Project of Guangxi Science and Technology Base and Talent (grant numbers GuiKe AD20297009 and GuiKe AD20297007), and the Middle-aged and Young Teachers' Basic Ability Promotion Project of Guangxi (grant numbers 2022KY0179, 2021KY0221, and 2020KY05039).

Institutional Review Board Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Martin, K.J.; Downing, L.S.; Nerenberg, R. Evidence of specialized bromate-reducing bacteria in a hollow fiber membrane biofilm reactor. *Water Supply* **2009**, *8*, 473–479. [CrossRef]
- Xiao, Q.; Yu, S. Reduction of bromate from drinking water by sulfite/ferric ion systems: Efficacy and mechanisms. *J. Hazard. Mater.* **2021**, *418*, 125940. [CrossRef] [PubMed]
- Yang, J.; Dong, Z.; Jiang, C.; Wang, C.; Liu, H. An overview of bromate formation in chemical oxidation processes: Occurrence, mechanism, influencing factors, risk assessment, and control strategies. *Chemosphere* **2019**, *237*, 124521. [CrossRef] [PubMed]
- Butler, R.; Ehrenberg, S.; Godley, A.R.; Lake, R.; Lytton, L.; Cartmell, E. Remediation of bromate-contaminated groundwater in an ex situ fixed-film bioreactor. *Sci. Total Environ.* **2006**, *366*, 12–20. [CrossRef]
- Jahan, B.N.; Li, L.; Pagilla, K.R. Fate and reduction of bromate formed in advanced water treatment ozonation systems: A critical review. *Chemosphere* **2021**, *266*, 128964. [CrossRef]
- Zhong, Y.; Yang, Q.; Fu, G.; Xu, Y.; Cheng, Y.; Chen, C.; Xiang, R.; Wen, T.; Li, X.; Zeng, G. Denitrifying microbial community with the ability to bromate reduction in a rotating biofilm-electrode reactor. *J. Hazard. Mater.* **2018**, *342*, 150–157. [CrossRef]
- Zhou, W.; Yang, Y.; Gai, W.-Z.; Deng, Z.-Y. A comparative study on high-efficient reduction of bromate in neutral solution using zero-valent Al treated by different procedures. *Sci. Total Environ.* **2021**, *795*, 148786. [CrossRef]
- Xia, S.; Liang, J.; Xu, X.; Shen, S. Simultaneous removal of selected oxidized contaminants in groundwater using a continuously stirred hydrogen-based membrane biofilm reactor. *J. Environ. Eng.* **2013**, *25*, 96–104. [CrossRef]
- Chen, X.; Liu, Y.; Peng, L.; Ni, B.-J. Perchlorate, nitrate, and sulfate reduction in hydrogen-based membrane biofilm reactor: Model-based evaluation. *Chem. Eng. J.* **2017**, *316*, 82–90. [CrossRef]

10. Jiang, M.; Zhang, Y.; Yuan, Y.; Chen, Y.; Lin, H.; Zheng, J.; Li, H.; Zhang, X. Nitrate removal and dynamics of microbial community of a hydrogen-based membrane biofilm reactor at diverse nitrate loadings and distances from hydrogen supply end. *Water* **2020**, *12*, 3196. [CrossRef]
11. Lai, C.-Y.; Lv, P.-L.; Dong, Q.-Y.; Yeo, S.L.; Rittmann, B.E.; Zhao, H.-P. Bromate and nitrate bioreduction coupled with poly-beta-hydroxybutyrate production in a methane-based membrane biofilm reactor. *Environ. Sci. Technol.* **2018**, *52*, 7024–7031. [CrossRef] [PubMed]
12. Martin, K.J.; Picioreanu, C.; Nerenberg, R. Assessing microbial competition in a hydrogen-based membrane biofilm reactor (MBfR) using multidimensional modeling. *Biotechnol. Bioeng.* **2015**, *112*, 1843–1853. [CrossRef] [PubMed]
13. Jiang, M.; Zheng, J.; Perez-Calleja, P.; Picioreanu, C.; Lin, H.; Zhang, X.; Zhang, Y.; Li, H.; Nerenberg, R. New insight into CO₂-mediated denitrification process in H₂-based membrane biofilm reactor: An experimental and modeling study. *Water Res.* **2020**, *184*, 116177. [CrossRef] [PubMed]
14. Tang, Y.; Zhao, H.; Marcus, A.K.; Krajmalnik-Brown, R.; Rittmann, B.E. A steady-state biofilm model for simultaneous reduction of nitrate and perchlorate, part 1: Model development and numerical solution. *Environ. Sci. Technol.* **2012**, *46*, 1598–1607. [CrossRef]
15. Downing, L.S.; Nerenberg, R. Kinetics of microbial bromate reduction in a hydrogen-oxidizing, denitrifying biofilm reactor. *Biotechnol. Bioeng.* **2007**, *98*, 543–550. [CrossRef]
16. Tang, Y.; Zhao, H.; Marcus, A.K.; Krajmalnik-Brown, R.; Rittmann, B.E. A steady-state biofilm model for simultaneous reduction of nitrate and perchlorate, part 2: Parameter optimization and results and discussion. *Environ. Sci. Technol.* **2012**, *46*, 1608–1615. [CrossRef]
17. Li, H.; Zhou, L.; Lin, H.; Zhang, W.; Xia, S. Nitrate Effects on Perchlorate Reduction in a H₂/CO₂-based Biofilm. *Sci. Total Environ.* **2019**, *694*, 133564. [CrossRef]
18. Lee, K.-C.; Rittmann, B.E. Applying a novel autohydrogenotrophic hollow-fiber membrane biofilm reactor for denitrification of drinking water. *Water Res.* **2002**, *36*, 2040–2052. [CrossRef]
19. Tang, Y.; Zhou, C.; Ziv-El, M.; Rittmann, B.E. A pH-control model for heterotrophic and hydrogen-based autotrophic denitrification. *Water Res.* **2011**, *45*, 232–240. [CrossRef]
20. Wu, J.; Yin, Y.; Wang, J. Hydrogen-based membrane biofilm reactors for nitrate removal from water and wastewater. *Int. J. Hydrogen Energ.* **2018**, *43*, 1–15. [CrossRef]
21. Estuardo, C.; Martí, M.C.; Huiliñir, C.; Aspé Lillo, E.; Roeckel von Bennewitz, M. Improvement of nitrate and nitrite reduction rates prediction. *Electron. J. Biotechnol.* **2008**, *11*, 73–82. [CrossRef]
22. Vavilin, V.A.; Vasiliev, V.B.; Rytov, S.V.; Ponomarev, A.V. Self-oscillating coexistence of methanogens and sulfate-reducers under hydrogen sulfide inhibition and the pH-regulating effect. *Bioresour. Technol.* **1994**, *49*, 105–119. [CrossRef]
23. Angelidaki, I.; Ellegaard, L.; Ahring, B.K. A mathematical model for dynamic simulation of anaerobic digestion of complex substrates: Focusing on ammonia inhibition. *Biotechnol. Bioeng.* **1993**, *42*, 159–166. [CrossRef] [PubMed]
24. Jiang, M.; Zhang, Y.; Zheng, J.; Li, H.; Ma, J.; Zhang, X.; Wei, Q.; Wang, X.; Zhang, X.; Wang, Z. Mechanistic insights into CO₂ pressure regulating microbial competition in a hydrogen-based membrane biofilm reactor for denitrification. *Chemosphere* **2022**, *303*, 134875. [CrossRef] [PubMed]
25. Tang, Y.; Ontiveros-Valencia, A.; Feng, L.; Zhou, C.; Krajmalnik-Brown, R.; Rittmann, B.E. A biofilm model to understand the onset of sulfate reduction in denitrifying membrane biofilm reactors. *Biotechnol. Bioeng.* **2013**, *110*, 763–772. [CrossRef]
26. Lv, X.; Wang, D.; Iqbal, W.; Yang, B.; Mao, Y. Microbial reduction of bromate: Current status and prospects. *Biodegradation* **2019**, *30*, 365–374. [CrossRef]
27. Pang, S.; Rittmann, B.E.; Wu, C.; Yang, L.; Zhou, J.; Xia, S. Synergistic inorganic carbon and denitrification genes contributed to nitrite accumulation in a hydrogen-based membrane biofilm reactor. *Bioengineering* **2022**, *9*, 222. [CrossRef]
28. Ghafari, S.; Hasan, M.; Aroua, M.K. Effect of carbon dioxide and bicarbonate as inorganic carbon sources on growth and adaptation of autohydrogenotrophic denitrifying bacteria. *J. Hazard. Mater.* **2009**, *162*, 1507–1513. [CrossRef]
29. Nerenberg, R. The membrane-biofilm Reactor (MBfR) as a counter-diffusional biofilm process. *Curr. Opin. Biotech.* **2016**, *38*, 131–136. [CrossRef]
30. Wang, F.; van Halem, D.; Ding, L.; Bai, Y.; Lekkerkerker-Teunissen, K.; van der Hoek, J.P. Effective removal of bromate in nitrate-reducing anoxic zones during managed aquifer recharge for drinking water treatment: Laboratory scale simulations. *Water Res.* **2018**, *130*, 88–97. [CrossRef]
31. Xia, S.; Xu, X.; Zhou, C.; Wang, C.; Zhou, L.; Rittmann, B.E. Direct Delivery of CO₂ into a Hydrogen-based Membrane Biofilm Reactor and Model Development. *Chem. Eng. J.* **2016**, *290*, 154–160. [CrossRef]
32. Henze, M.; van Loosdrecht, M.C.; Ekama, G.A.; Brdjanovic, D. *Biological Wastewater Treatment*; IWA Publishing: London, UK, 2008.
33. Lide, D.R. *CRC Handbook of Chemistry and Physics*; CRC: Boca Raton, FL, USA, 2012.



Review

A Critical Review of Renewable Hydrogen Production Methods: Factors Affecting Their Scale-Up and Its Role in Future Energy Generation

Ephraim Bonah Agyekum ^{1,*}, Christabel Nutakor ², Ahmed M. Agwa ^{3,4,*} and Salah Kamel ⁵

¹ Department of Nuclear and Renewable Energy, Ural Federal University Named after the First President of Russia Boris Yeltsin, 19 Mira Street, 620002 Ekaterinburg, Russia

² Department of Biochemistry and Forensic Science, C. K. Tedam University of Technology and Applied Sciences, Navrongo P.O. Box 24, Ghana; nutakor.christabel@gmail.com or cnutakor@cktutas.edu.gh

³ Department of Electrical Engineering, College of Engineering, Northern Border University, Arar 1321, Saudi Arabia

⁴ Prince Faisal bin Khalid bin Sultan Research Chair in Renewable Energy Studies and Applications (PFCRE), Northern Border University, Arar 1321, Saudi Arabia

⁵ Electrical Engineering Department, Faculty of Engineering, Aswan University, Aswan 81542, Egypt; skamel@aswu.edu.eg

* Correspondence: agyekumephraim@yahoo.com or agyekum@urfu.ru (E.B.A.); ah1582009@yahoo.com (A.M.A.)

Abstract: An increase in human activities and population growth have significantly increased the world's energy demands. The major source of energy for the world today is from fossil fuels, which are polluting and degrading the environment due to the emission of greenhouse gases. Hydrogen is an identified efficient energy carrier and can be obtained through renewable and non-renewable sources. An overview of renewable sources of hydrogen production which focuses on water splitting (electrolysis, thermolysis, and photolysis) and biomass (biological and thermochemical) mechanisms is presented in this study. The limitations associated with these mechanisms are discussed. The study also looks at some critical factors that hinders the scaling up of the hydrogen economy globally. Key among these factors are issues relating to the absence of a value chain for clean hydrogen, storage and transportation of hydrogen, high cost of production, lack of international standards, and risks in investment. The study ends with some future research recommendations for researchers to help enhance the technical efficiencies of some production mechanisms, and policy direction to governments to reduce investment risks in the sector to scale the hydrogen economy up.

Keywords: hydrogen production; biomass; proton exchange membranes; alkaline electrolysis; dark fermentation; anion exchange membranes

1. Introduction

The increase in energy demand globally has led to an increase in discussions around clean, cheap, and sustainable sources of energy generation [1–3]. The global population has been estimated to hit a possible 10 billion people by 2050, which is expected to have an exponential effect on energy requirements. The use of fossil fuels as a source of energy generation has helped transform economies around the world but at a negative cost to the environment. It is for this reason, among other reasons, that researchers and scientists are investigating various forms of energy generation that comes with a zero or lower negative effect on the environment [4–7].

One of the alternatives to the conventional forms of energy generation is the use of 'green' hydrogen. This comes with no emissions of greenhouse gases (GHG) provided the process is done using power from renewable sources (RS). The facile electrochemical conversion, light weight, and high mass energy density of hydrogen enables it to carry

energy across geographical areas in the form of liquid fuels, with freight ships or through pipelines [8]. The hydrogen atom is generally made up of a proton and an electron, and it is colorless and odorless. Its density is lower than that of air. Hydrogen's energy gravimetric density is largely about seven times higher than that of fossil fuels [9]. Moreover, 1.0 kg of hydrogen is estimated to have a storage energy that is more than 2.75 kg that of gasoline. As a result, a liter of hydrogen has same energy as 0.25 L of gasoline [10].

As indicated above, hydrogen is produced through the conversion of materials which contain the hydrogen element, for example, carbohydrates or water. It is valued that close to 96% hydrogen worldwide is gotten from conventional fossil fuels divided as follows: 30% from naphtha reforming, 48% from steam reforming of natural gas, and 18% from coal gasification [10]. The conventional technologies used for the production of hydrogen, however, are linked to the environmental pollutions being experienced worldwide. It is for this reason that people in the energy and environment sector are pushing for more sustainable ways of producing hydrogen using RS.

Hydrogen products are currently being used as raw materials in the industrial sector. However, if we are to realize its full potential as a full energy carrier, it can play a major part in many more areas. Out of the estimated 50 million metric tons produced yearly on a global scale, its main use is as a feedstock for the production of ammonia, with oil refining taking 35% [11]. It could have major application in the freight and passenger transport (i.e., internal combustion engines and fuel cell vehicles), storage (gaseous or liquid hydrogen), thermal (natural gas blending and solid oxide fuel cells) [11,12], electricity generation and power to gas generation [13], upon realizing its role as a flexible energy carrier, etc., as shown in Figure 1.

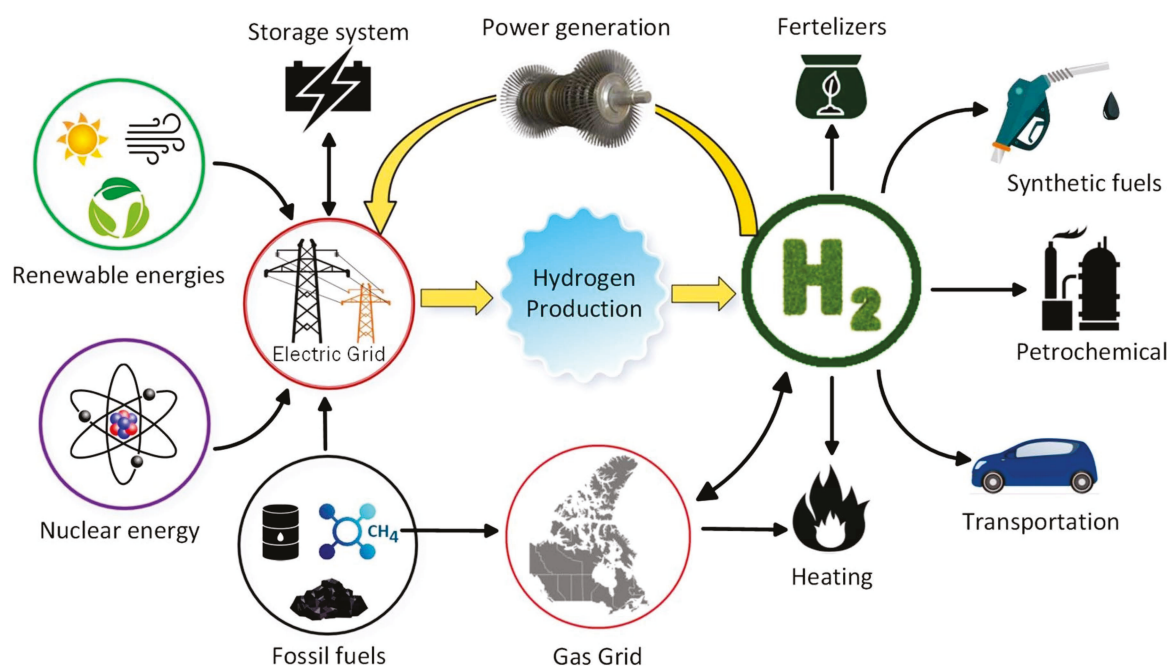


Figure 1. Effect of hydrogen production on other sectors [14]. Reproduced with permission from Elsevier, 2022.

Yue et al. [15] presented a review on recent developments of technologies on hydrogen and their application in power systems for the production of hydrogen, storage, and re-electrification. Dawood et al. [16] also reviewed various hydrogen production pathways to assess their interrelationship and interconnection on other stages of the hydrogen square. A study by Najjar [17] reviewed the safety of hydrogen in the course of production, transmission, and usage but did not look at various limitations associated with the various technologies for the production of hydrogen. According to their study, safety issues in

relation to hydrogen use are mostly discussed in relation to its ignition and combustion features, i.e., low ignition energy, rapid diffusion, comparatively high flame velocity, extensive flammability range explosion level, etc. Parra et al. [18] evaluated the progress of hydrogen production from the perspective of cost; however, it lacked a detailed assessment of the various trends of the development of the various technologies. Kovac [19] reviewed hydrogen in energy transition. According to the study, this is important because the world is fast changing, which has led to discussions around technological advancement among the people. The study presented the progress being made in the hydrogen sector. Maggio et al. [20] reviewed how the production of hydrogen from renewable energy sources could affect the fuels markets. Their study suggests that producing hydrogen through electrolysis will have a significant economic impact, particularly in the area of transport, which will lead to the creation of new supply chain, and market, which will change the characteristics of the energy market. Hanley et al. [11] provided a review of hydrogen production through low-carbon methods from varying integrated energy system models. Their objective was to identify the policy scenarios and factors that lead to the advent of hydrogen over other low carbon technologies. They identified that bioenergy could serve as both a driver and competitor for hydrogen energy, along with high renewable electricity scenarios and increased electrification. Electric vehicles were, however, identified as the key competitor in the passenger vehicle sector. Additionally, Abe et al. [21] presented a short overview of hydrogen as an energy carrier. The study identified the storage of hydrogen as a hinderance to its development and provided some recommendations for its development.

Finally, Liu et al. [22] looked at the trends and future challenges for the production and storage of hydrogen. According to their findings, the most researched hydrogen production mechanism during their study period, i.e., 2004–2018, is the photocatalytic decomposition of water to hydrogen. Mengdi and Wang [23] recently provided an overview of technologies use for the production of hydrogen, which includes both renewable and non-renewable resources. They also compared the life cycle environmental impact assessment for the various technologies. Hosseini and Wahid. [24] also looked at various hydrogen production technologies. Their findings indicate that the high cost of photovoltaic cells and their low efficiency are the most critical barriers for the commercialization of solar based hydrogen production. Similarly, El-Emam and Ozcan [25] provided an analysis on the economic, technological, and environmental aspects of hydrogen production. They observed that the lower cost of electricity that is associated with geothermal and nuclear energies makes them the ideal sources for the production of hydrogen at low-cost. Okonkwo et al. [26] conducted a study on the possibility of producing, using and exporting carbon-free hydrogen from Qatar. The findings of their paper shows that the best pathway for Qatar at present is the production as well as exportation of blue ammonia, whereas green hydrogen could in the mid-future become as competitive as blue ammonia. In another study, Lane et al. [27] forecasted renewable production of hydrogen technology shares. The outcome of the study suggests that the dominant technology consists of biomass gasifiers on the early market; however, electrolyzers' higher learning rate as well as the long-term trend of declining cost for RE could lead to equal shares for installations that are new by mid-term and ultimately to electrolyzers having the leading share of new facilities.

In this paper, a review of clean hydrogen production technologies is presented. This is not the first time the different hydrogen production technologies have been discussed, as there have been some studies, discussed in previous sections, and some of these [28–31] have reviewed one or more forms of the processes associated to hydrogen production. Aside from the emphasis on clean technologies in this paper, it also moves beyond the review of the technologies alone and presents the limitations associated with them. Challenges in the sector that is hindering the progress of the hydrogen economy globally are also presented. The role of hydrogen in the world's energy sector is also presented.

2. Status of the Global Hydrogen Production

According to the International Energy Agency (IEA) [32], technologies for the production of hydrogen were unusually robust during the COVID-19 pandemic, with their momentum in 2020 remaining strong. According to the IEA report, the year 2020 was a record year in policy action and low-carbon production, where a total of ten governments across the globe adopted hydrogen strategies. An installation of about 70 MW capacity of electrolysis was done, which doubled the preceding year's record, and two hydrogen producing facilities from fossil fuels with Carbon Capture, Utilization, and Storage (CCUS) became operational, which led to about a 15% increase in production capacity [32]. Reports show that the global total hydrogen demand has increased rapidly by 27.2% in 7 years, i.e., from 255.3 billion cubic meters in 2013 to some 324.8 billion cubic meters in 2020 [33,34]. Figure 2 shows the increase in demand for H₂ over the years; it can be seen that the produced hydrogen are mostly used in the production of ammonia (51%), while about 31% goes into oil refining, 10% is used for the production of methanol, and the remaining 8% has other uses [35].

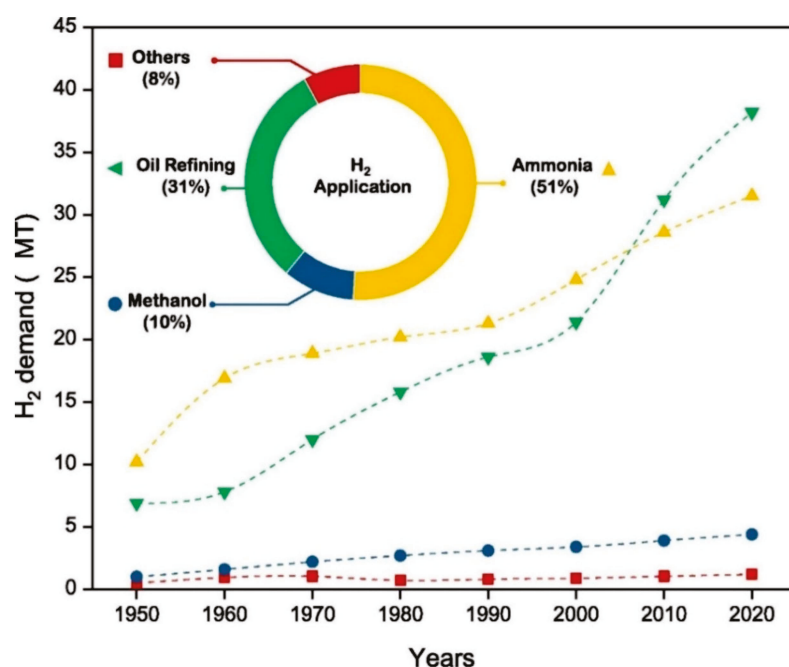


Figure 2. Demand of hydrogen worldwide and its share on various uses [35]. Reproduced with permission from Elsevier, 2022.

The hydrocarbon steam reforming is presently the most utilized approach for the production of hydrogen globally, it is used in over 90% of industrial hydrogen production facilities. It is a technology that was invented in 1926 by the Badische Anilin-und-Soda-Fabrik (BASF) [34,36].

Reports by the Hydrogen Council and McKinsey & Company [37] indicated that out of the 228 large-scale industrial, infrastructure, and transport hydrogen projects around the world, more than half, i.e., 126, are projected to be sited in Europe, 19 in North America, 24 in the Oceania, and 46 in Asia. These projects are estimated to be a potential investment of 1.4% of the global energy fund, which is equivalent to \$300 billion. According to the same report, a total of 75 countries around the world, which translates into more than half of the world's gross domestic product (GDP), have instituted net-zero carbon ambitions and over 30 have strategies directed at hydrogen production.

3. Paths to Hydrogen Production

Production of hydrogen is mainly done using either fossil fuels or through RS, which is presented in Figure 3. The widely used approach is called “steam reforming”. Methane is the widely used fuel in this process due to its high hydrogen-to-carbon ratio within the hydrocarbons group; therefore, the generated by-products are reduced [38]. The steam methane reforming (SMR) process is generally made up of two steps, as presented below [39]:

- The initial step is the reformation process; at this stage, there is the mixing of the methane with steam, which is moved over a catalyst bed with a high pressure of 1.5–3 MPa and a temperature range of 700–900 °C to form a combination of carbon monoxide (CO) and hydrogen, as presented in Equation (1).
- The next phase involves the shift reaction, where there is the reaction of additional steam with the CO from the initial phase to produce additional hydrogen and CO₂, as indicated in Equation (2):

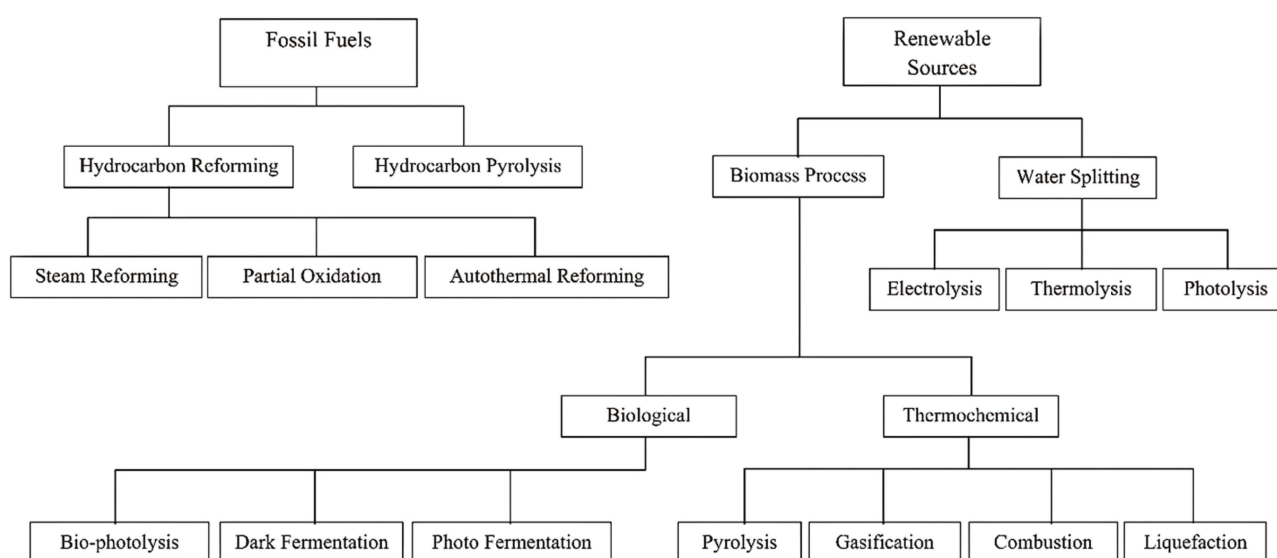


Figure 3. Routes to hydrogen production [28,40]. Reproduced with permission from Elsevier, 2022.

Coal gasification is the other method for the generation of hydrogen that uses fossil fuels. In this method, the coal is taken through a partial oxidation at high pressure, approximately 5 MPa, and temperature with the assistance of steam and oxygen to yield a combination of CO, methane, CO₂, and other compounds [41]. Hydrogen and CO mostly remain at temperatures beyond 1000 °C and pressures of 1 bar. The process is presented in Equations (3) and (4) [39]:



This study, however, only focuses on the various renewable (RE) options and discusses them in detail in subsequent sections below. A review of recent studies using different methodologies are presented in Table 1.

Table 1. Recent studies on the production of hydrogen.

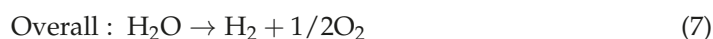
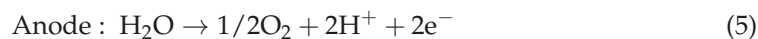
No.	Year	Mechanism Used	Objective of Study	Major Findings/Results	Ref.
1	2017	Thermo-electrochemical production protonic membrane reformer	To obtain high-purity hydrogen within a single-stage process in an almost zero energy loss.	The study achieved a balanced thermal operating regime. A total energy efficiency more than 87% was obtained for the modeled hydrogen plant.	[42]
2	2021	Alkaline water electrolysis	To investigate the effect of electrode spacing on the production of hydrogen.	It was identified that smaller spacing distances for electrodes increases the interaction between the immersed electrode and the ionic electrolyte, which increases the rate of the electrochemical reaction, efficiency, and production of hydrogen.	[43]
3	2021	Proton exchange membrane electrolysis cell (PEMEC)	To assess the performance of PEMEC, which is operated by a photovoltaic thermal (PVT) system. It assessed the impact of thermoelectric generator (TEG) and phase change materials (PCM) on the production of hydrogen.	A combination of the PVT/TEG/PEMEC system performed better than other systems. The PVT/PEMEC/PCM system recorded negligible effect.	[44]
4	2019	Evaluation of solar driven natural gas reforming system	To assess the impact of a combination of steam methane reforming with carbon dioxide as well as steam-based autothermal reforming.	There was an improvement in both exergy and energy efficiencies. The exergy efficiency is 31.1%, while the energy efficiency is 59.1%.	[45]
5	2021	Photo fermentation	To assess the role of catalysts in energy conversion efficiency enhancement and the yield of photo-fermentation biohydrogen from a corn stalk (CS) via strengthening the beneficial metabolic product.	The hydrogen yield was increased by 15.93% when 0.2 g/g CS of kieselguhr was added to the liquid culture.	[46]
6	2011	Photoelectrochemical	To investigate the hydrogen evolution rate for a photoelectrochemical system, which consists of platinum as a photoanode and cathode, and anodized tubular TiO ₂ , solar cell, as well as seawater, which is prepared using a nanofiltration membrane.	The rate hydrogen evolution was found to be 270 mol/cm ² h.	[47]
7	2021	Bio-hydrogen production based on lignocellulosic biomass	To explore the syntrophic co-fermentation model for microbial community evolution evaluation and the route of carbon transfer for the co-fermentation system.	The highest level of hydrogen production is 165 mL/g with a mean hydrogen concentration of 52.3%.	[48]
8	2021	Water electrolysis, electrochemical conversion	To propose an efficient strategy to replace the oxygen evolution reaction with a partial oxidation of degradation products originating from carbohydrate.	The results indicate that there exists the potential to use industrial waste streams for sustainable hydrogen production.	[49]
9	2019	Proton exchange membrane	To propose a synthesized polybenzimidazole (PBI) composite membrane from the addition of zirconium oxide (ZrO ₂) followed with phosphoric acid.	The efficiency of the copper chloride (CuCl) electrolyzer ranged from 91–97%, which indicates that the hybrid PBI/zirconium phosphide (ZrP) membrane can serve as an alternative to the Nafion membrane.	[50]

3.1. Water Splitting

Water is seen as the most abundant source for the production of hydrogen, which is made up of hydrogen and oxygen. Therefore, if sufficient energy is given to it, its molecules will split into hydrogen and oxygen. Several technologies can be adopted to split the water. Some of these technologies are discussed in detail in the subsections below.

3.1.1. Electrolysis of Water for the Production of Hydrogen

In this process, the reactant is water, which is dissociated into oxygen and hydrogen using DC current:



There are different electrolyte systems that can be used for water electrolysis, which includes anion exchange membranes (AEMs) electrolysis, alkaline water electrolysis (AWE), solid oxide water electrolysis (SOE), and proton exchange membranes (PEMs) electrolysis. They operate using same principle, although they operate under different conditions using different materials [51].

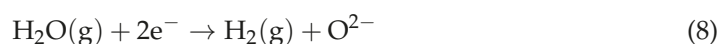
Alkaline Water Electrolysis

This method makes use of two non-platinum group metals, i.e., nickel (Ni) and iron (Fe) based electrodes, 30–40% potassium hydroxide (KOH) electrolyte, and a diaphragm membrane. Alkaline electrolysis is seen as a technology that is reliable for hydrogen production up to the megawatt scale [52,53]. The alkalinity is provided by the circulating KOH electrolyte. The permeable diaphragm plays the role of a separator to separate the cathode and the anode. It also plays the following roles: conduction of hydroxyl ions, ensuring safety and efficiency, and prevention of possible gas crossover [52–54]. Organic polymers, such as polypropylene, as well as ceramic oxide materials, e.g., potassium titanate and asbestos, can be used for the construction of the diaphragm [55].

A typical AWE works at a current density that ranges from 300–400 mA cm⁻², with a cell voltage that ranges from 1.85–2.2 V, moderate temperature of 70–90 °C, and conversion efficiencies ranging from 60–80%. The merits of this technology are that it is independent of a noble metal catalyst for the production of hydrogen, and its relatively low temperature makes its handling easier [56].

Solid Oxide Water Electrolysis

This is an innovative concept which allows water or steam electrolysis at temperatures that range from 600–900 °C. Higher efficiencies are obtained in this approach compared to the PEM and alkaline electrolyzers. Both recycled hydrogen and steam are supplied to the cathode; water is then reduced to yield hydrogen, as indicated in Equation (8). The oxide anions produced at the cathode goes through the solid electrolyte to the anode, and at this stage, they recombine to form oxygen and closes the circuit with the electrons released, as indicated in Equation (9) [52]:



In this concept, the reaction changes with the electrodes in contact with the vapor phase or gas, which is a clear deviation from the processes that takes place on the electrodes of the PEM or alkaline electrolyzers. This makes it challenging to maximize the interfacial area which is in contact between the gaseous chemical species and electrodes [52]. Figure 4 shows the water and steam electrolysis energy demand.

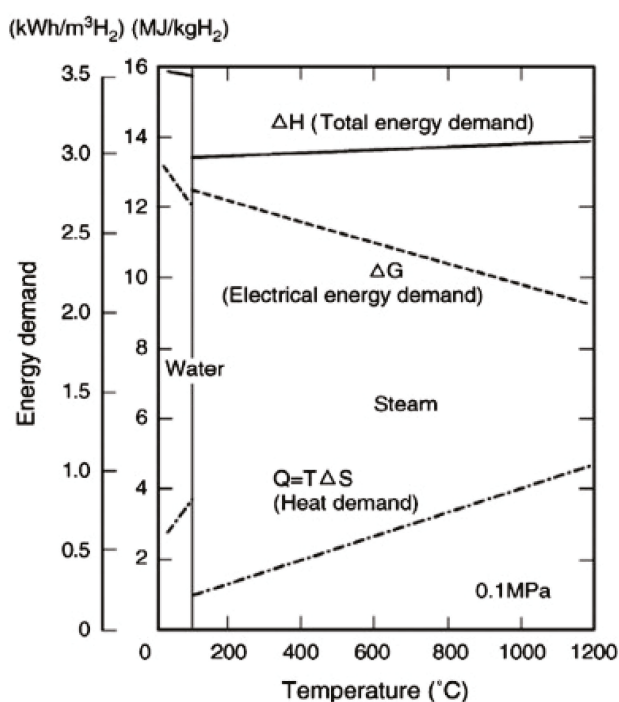


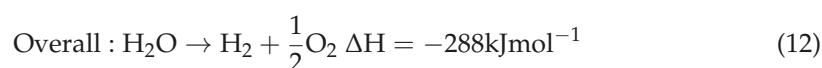
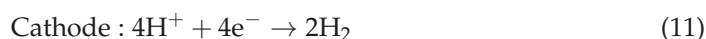
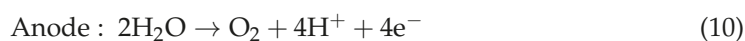
Figure 4. Water and steam electrolysis energy demand [57]. Reproduced with permission from Elsevier, 2022.

Proton Exchange Membranes

PEM is mostly employed in fuel cells for electricity generation and in electrolyzers for hydrogen production. It also serves as a separator between the cathode and the anode. The most used PEMs are the NafionTM and NafionTM-based membranes as a result of their high thermostability, high ionic conductivity, excellent chemical stability, good mechanical strength, and robustness at a low temperature during high levels of relative humidity [58]. There are, however, some major challenges associated with the use of the NafionTM, i.e., poor proton conductivity when temperatures are high under low humid environment and longer time needed for synthesis [58–60].

In PEM electrolyzers, there is the introduction of water at the anode where splitting into proton and oxygen occurs. The proton then moves to the cathode through the membrane, where recombination occurs to form hydrogen [61]. The oxygen gas is left behind with the unreacted water. A drier may be employed to eliminate residual water depending on the requirements for purity after the liquid/gas separations unit. There is a low ionic resistance in PEM electrolyzers; hence, a high current greater than 1600 mA cm² can be attained, while high efficiencies of 55–70% is maintained.

The cathode and anode reactions are presented below [61]:



Anion Exchange Membranes

The AEM method is a hybrid technique (i.e., in relation to water electrolysis), which integrates the merit of alkaline and PEM electrolysis within a cell, which consists of an AEM that is hydrocarbon-based and two transition metals, for example platinum (Pt), iridium (Ir), etc., of catalyst-based electrodes [62]. Figure 5 shows the process of AEM and the components involved. There is a connection of an external power supply to the cathode

and anode for the provision of DC current. The entire reaction is made up of two half-cell reactions, i.e., oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER). Water is passed through the side of the anode, which produces hydrogen and hydroxyl ions through the adding of two electrons. Then, there is the diffusion of the hydroxyl ions through the AEM to the portion of the anode through the positive attraction of the anode, whereas through the external circuit the electrons move to the anode. The hydroxyl ions recombine in the anode chamber as oxygen and water through the loss of electrons. The oxygen is released from the anode's surface by forming bubbles. Catalytic activity is required by both half-cell reactions for the formation and emission of the corresponding gases from the surfaces of the electrode. The half-cell reactions in Equations (13)–(15) apply [56,63]:

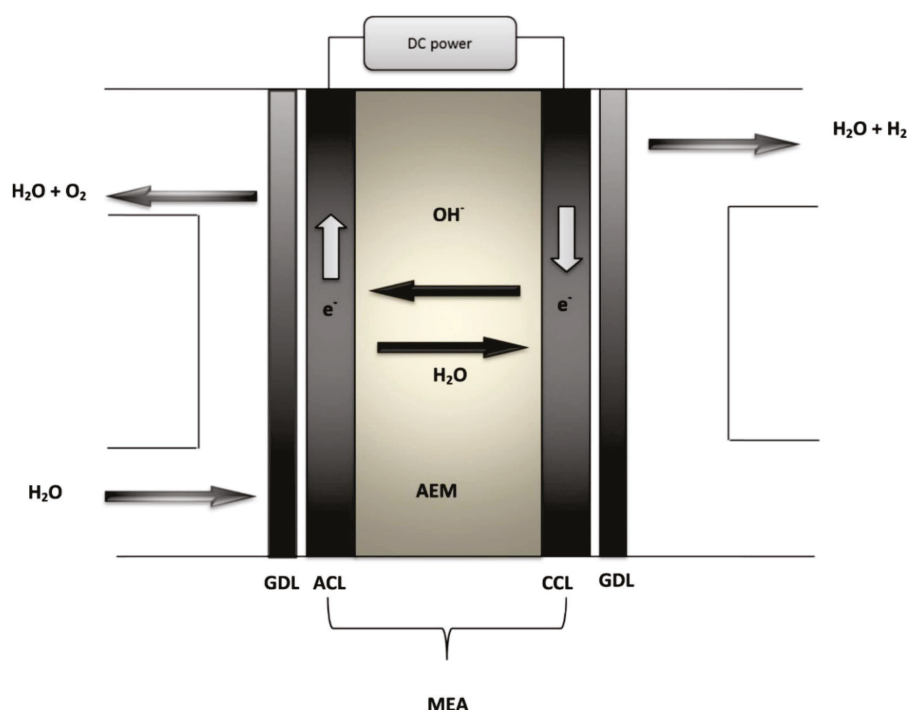
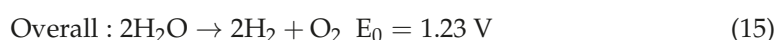
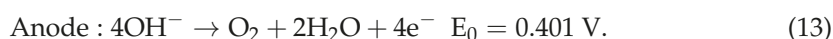


Figure 5. Diagram of an AEM water electrolysis. CCL: cathode catalyst layer, ACL: anode catalyst layer, GDL: gas diffusion layer, and MEA: membrane electrode assembly [56]. Reproduced with permission from Elsevier, 2022.

The reaction needs a theoretical thermodynamic cell voltage of 1.23 V at a temperature of 25 °C in order to dissociate the water into hydrogen and oxygen. However, in practice, in order to obtain an efficient hydrogen production, the cell voltage must be greater than 1.23 V. Extra voltage is needed to overcome the ohmic resistance and the kinetics of the electrolyte as well as the electrolyzer's components [56].

3.1.2. Thermolysis of Water for Production of Hydrogen

The thermolysis of water, which is referred to as a single stage thermal dissociation of water, is presented as follows [64]:



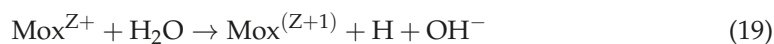
The reaction in this approach requires a source of heat to be able to get a reasonable level of dissociation; this heat source should be able to make available temperatures beyond 2500 K. For example, the level of dissociation at 3000 K and 1 bar is 64% [64]. These are the main challenges associated with this method of production. Another challenge associated with this form of hydrogen production is the high cost of its equipment due to the need to withstand the high conditions presented earlier in this section. Different technologies are, therefore, being proposed in order to conduct thermolysis at lesser temperatures. One of such strategies involves the conduction of the reaction in a number of phases with the use of catalysts; however, the requirement of very corrosive reagents also poses challenges to equipment as well as a possible negative impact on the environment [65].

Kasai and Bishop [66] proposed a single reaction system, which can realize an entropic exchange for the production of hydrogen through thermolysis by means of zeolites. Free hydrogen as well as oxidize bivalent cations are produced from the rehydration of zeolites, which happens at temperatures around 400 °C. In the same way, Hsu [67] proposed a raney nickel plate reactor (10% Aluminum and 90% Nickel), which functions as a catalytic surface to change the reaction's energy activation. Additionally, iodine (I₂) and sulfur dioxide (SO₂) were added to the medium, which had a decreasing effect on the temperature of the reaction, as presented in Equations (17) and (18) [65]:



3.1.3. Photolysis of Water for Hydrogen Production

Water can release hydrogen in principle, which occurs when the water molecules absorb energy at a rate of 285.57 kJ/mole of water from ultraviolet radiation [68]. The dissociation of the H-O bonds by photons is known as photolysis, which occurs at about 190 nm [69]. This process and thermolysis need chemical catalysts such as ZrO₂, tin oxide (SnO), zinc oxide (ZnO), and other semiconductor sulfur oxides [65] (Equations (19) and (20)):



3.1.4. Some Limitations Associated with Water Electrolysis Technologies

Some limitations associated with some of the technologies presented above are presented below [70]:

- Solid oxide electrolysis—requires a relatively large laboratory stage, low durability, and large system design.
- PEM electrolysis—has an acid environment, immature and costly components, and low durability.
- Alkaline electrolysis—has low current densities, purity of gases is low, low dynamic operation, operational pressure is low (3–30 bar), and there is a reduction in the electrolyzers performance due to the formation of carbonates on the electrode.

3.2. Biomass Process of Hydrogen Production

Biomass is seen as more promising compared to fossil fuels in terms of hydrogen production due to its large reserves and supply, easy oxidation, and high annual output. Therefore, hydrogen can be produced in various forms in relation to biomass as shown in Figure 6. This includes thermochemical conversion of wood waste, photocatalysis (PC) of municipal solid waste, lignin, sawdust, forest residues, agricultural waste, cellulose, polyols, fermentation of microalgae and cassava, biomethane (biogas), steam reforming of gasified biomass tar, etc. [34]. Even though there is a release of CO₂ during the production of hydrogen using biomass, the quantity of gaseous emissions is equal to the quantity ab-

sorbed by organisms during their lifetime [71]. Biological and thermochemical mechanisms are the two approaches that can be used to produce hydrogen from biomass. These will be discussed in subsequent sections.

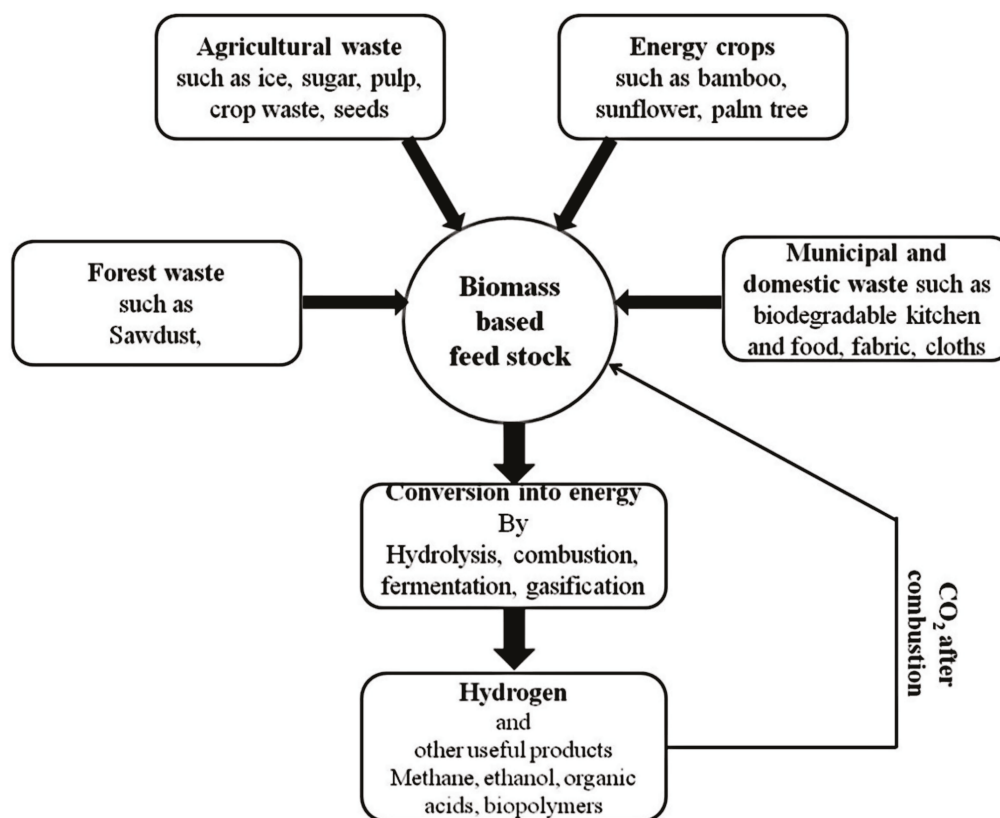


Figure 6. Sources of biomass and their conversion into hydrogen and other beneficial products [72]. Reproduced with permission from Elsevier, 2022.

Different from coal, biomass has a comparatively high hydrogen-to-carbon ratio. It is estimated that $C_6H_{10}O_5$ (pure cellulose) has a hydro-carbon ratio of approximately 1.7 as compared to that of 0.8 for a characteristic bituminous coal [73]. Using biomass can decrease the dependence on hydrocarbons. Biomass can fix CO_2 balance in the atmosphere through a mechanism known as photosynthesis process [74].

3.2.1. Biological Production

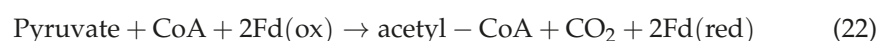
Dark Fermentation Process of Hydrogen Production

Dark fermentation (DF) is seen as the most promising technique for the generation of biohydrogen via the conversion of biomass, it has a net energy ratio equivalent to 1.9, while that of steam methane reforming is equal to 0.64 [75]. Production of hydrogen can be done by anaerobic bacteria, which are grown in carbohydrate rich or dark substrate. The anaerobic metabolism of pyruvate, which is formed due to the catabolism of various substrates, drives most microbial hydrogen production. One of two enzyme systems catalyze pyruvate breakdown [75]:

1. *Pyruvate: formate lyase:*



2. *Pyruvate: ferredoxin oxido reductase:*



Substrates in DF are transformed by anaerobic bacteria grown in the dark (Figure 7). The key substrate in metabolism is hydrogen for several anaerobic microorganisms. If they are available, such microorganisms are capable of utilizing hydroenergy-rich hydrogen molecules, to produce energy through the use of the electrons from the hydrogen oxidation. When there are no external acceptors of electrons, the organisms have extra generated electrons in the process of metabolism due to the reduction of protons producing hydrogen molecules. Hydrogenases are the key enzymes that regulate hydrogen metabolism [76].

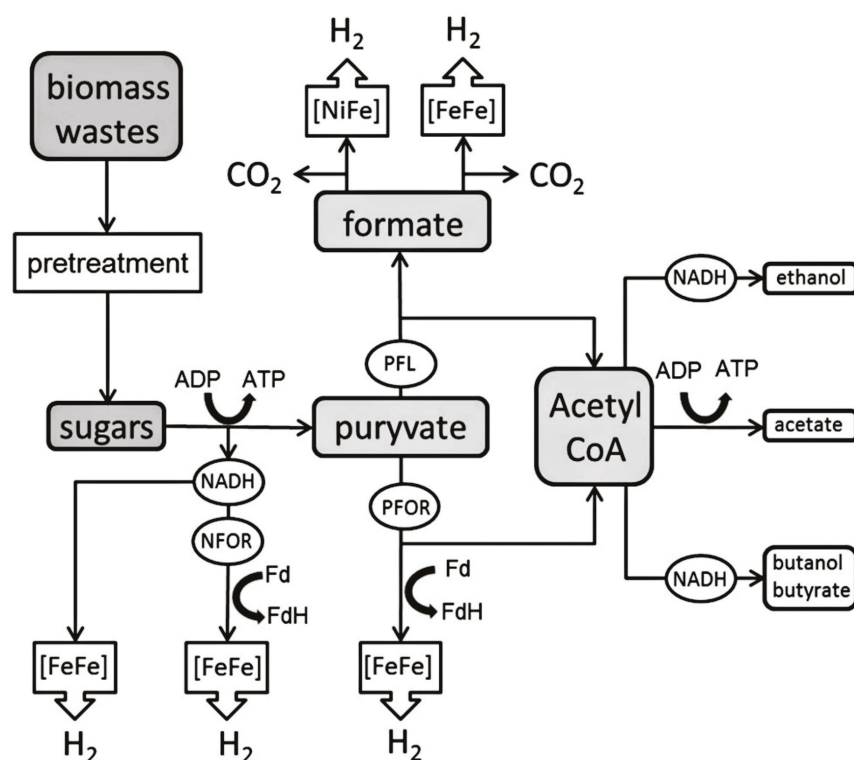


Figure 7. Characteristic metabolic ways for converting substrate to hydrogen during DF [76]. Reproduced with permission from Elsevier, 2022.

Photo Fermentation Process of Hydrogen Production

Photo fermentation is considered as one of the probable pathways for the production of biological hydrogen. Anoxygenic photosynthetic bacteria, especially the purple non-sulfur (PNS) bacteria, are in this process able to reduce H^+ ions to gaseous H_2 , through the use of both the reduction power obtained from the organic compounds' oxidation, e.g., low-molecular weight fatty acids as well as light energy. This mechanism is regarded as promising as a result of the absence of O_2 -evolving reactions, the potential to utilize varied range of sunlight, high substrate conversion yields, and the potential to combine this form of H_2 production methods with waste disposal [77].

Rhodobacter, a PNS bacterial genus, is the most commonly used for the production of biohydrogen. PNS bacteria can grow photo-heterotrophically and acquire their carbon needs and electrons from reduced fixed carbon compounds, using CO_2 as the only source of carbon and H_2 , S_2 , or Fe^{2+} as electron donors, while some species can also grow photo-lithoautotrophically. The PNS can utilize a variety of organic carbon compounds: amino acids, alcohols and carbohydrates, acetate, and other organic acids and pyruvate depending on the species. Other species can also utilize compounds with a one-carbon atom, such as formate and methanol, whereas others grow with the use of aromatic organic compounds, e.g., chlorobenzoate, cinnamate, benzoate, phenol, and phenylacetate [78]. Figure 8 shows the production of hydrogen through photo-fermentation.

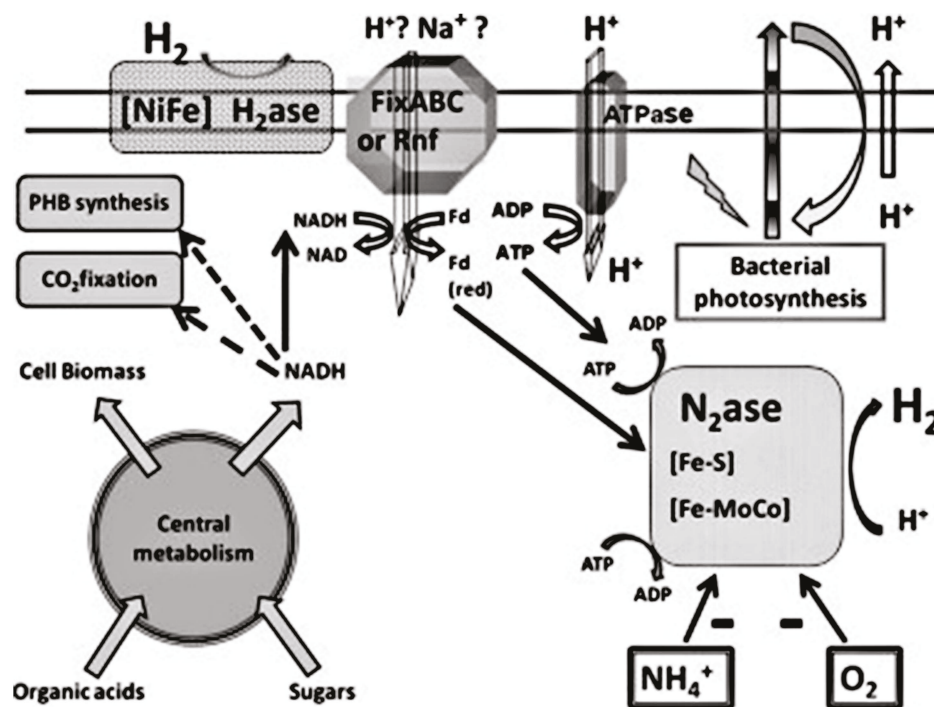


Figure 8. Production of hydrogen via photo-fermentation through photosynthetic bacteria paths, resulting in the production of hydrogen via a non-sulfur-deprived photosynthetic bacterium [78]. Reproduced with permission from Elsevier, 2022.

The reaction for the production of hydrogen using photo fermentative mechanism using acetate is presented in Equation (23). The reaction is not spontaneous due to its positive free energy and as a result requires external energy in the form of light (natural or artificial). Four moles of hydrogen can be theoretically produced from the 1 mol of acetate under adequate physico-chemical conditions [79].



Bio-Photolysis Process of Hydrogen Production

This is a biological process that employs similar principles that are seen in algae and plants photosynthesis which are adapted for the production of hydrogen gas. Only carbon dioxide reduction occurs in green plants, as there is an absence of the enzyme that catalyze the formation of hydrogen. However, there exist hydrogen-producing enzymes in algae which can produce hydrogen under certain situations [80]. Bio-photolysis can take place in either directly or indirectly form under illumination, which then results in H₂ and O₂ production [81].

The most analyzed species for direct bio-photolysis is the microalgae *Chlamydomonas reinhardtii*. Both photosystems (PSI and PSII) and hydrogenase enzymes play active roles in direct bio-photolysis [82]. The molecules of water are split by green algae in direct bio-photolysis to form oxygen and hydrogen ion via photosynthesis. H₂ is produced through the conversion of the generated hydrogen ions by hydrogenase enzyme. This enzyme is extremely sensitive to oxygen, and as a result, the oxygen content must be maintained below 0.1%, which is a drawback of this technology [83]. The process of direct bio-photolysis is presented Figure 9.

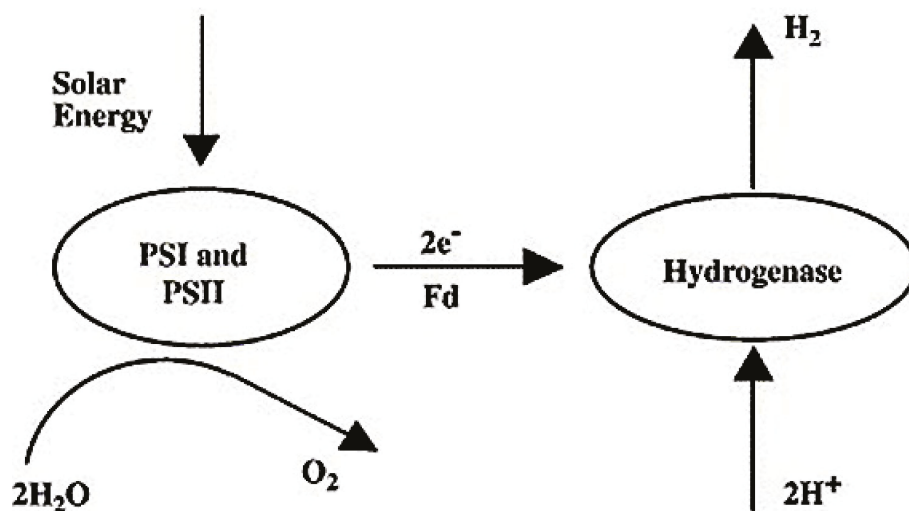


Figure 9. Representation of direct bio-photolysis [83]. Reproduced with permission from Elsevier, 2022.

Indirect bio-photolysis could be used with many of the cyanobacteria. In this case, the process of the photosynthesis is accompanied by dark fermentation to produce H_2O and H_2 . The conversion of CO_2 into an endogenous reserve carbohydrate occurs before the production of hydrogen in the presence of hydrogenase enzyme [82,84]. Figure 10 illustrates the indirect mechanism of the production of hydrogen. The indirect bio-photolysis concept can be divided into four groups [83]:

- Production of biomass via photosynthesis.
- Biomass concentration.
- Aerobic DF producing 4 mol hydrogen/mol glucose in algae cell, accompanied by 2 mol of acetates.
- Production of hydrogen through the conversion of 2 mol of acetates.

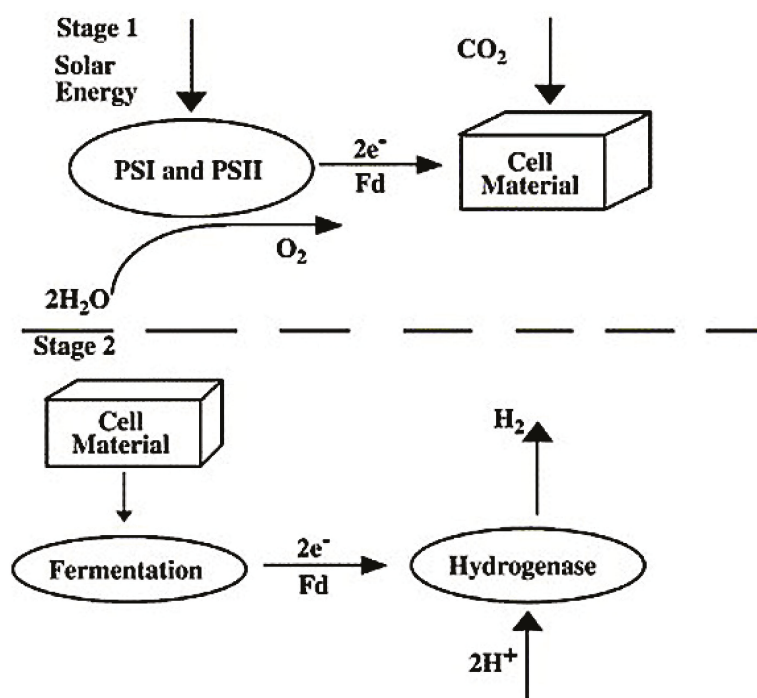
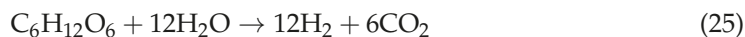


Figure 10. Production of hydrogen using an indirect bio-photolysis approach [83]. Reproduced with permission from Elsevier, 2022.

Cyanobacteria are used in a typical indirect bio-photolysis to produce hydrogen through the reactions provided in Equations (24) and (25):

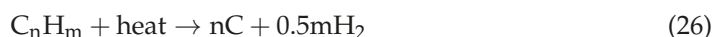


3.2.2. Thermochemical Production

The thermochemical method is a system whereby biomass is converted into hydrogen rich gases and hydrogen. The production of hydrogen-rich gases from synthesis gas obtained from such methods is seen as the way forward for zero GHG emissions, which is necessary for sustainable development [28,85]. The thermochemical method is mainly made up of gasification and pyrolysis. The two conversion methods produce CH_4 and CO , among other gaseous products, which can be treated more for the production of additional hydrogen through water gas shift (WGS) and steam reforming reaction. Liquefaction and combustion methods are additional mechanisms that are two less preferable approaches, since they produce low hydrogen with the release of byproducts and also requiring operating conditions of 5–20 MPa without the presence of air, which are difficult to meet [83].

Pyrolysis Way of Hydrogen Production

Pyrolysis or co-pyrolysis is another promising technique for the production of hydrogen. In this technique, heating and gasification of raw organic material occur in a temperature range of 500–900 °C at a pressure of 0.1–0.5 MPa [86,87]. The process happens in the absence of air and oxygen, and consequently, the formation of dioxins can be ruled out. The absence of air or water means there will be no formation of carbon oxides (CO_2 and CO) to require secondary reactors. As a result, this process of hydrogen production helps to reduce emissions. However, in the situation where there is the presence of water or air (i.e., the materials are not dried), there will be significant emission of CO_x . Some of the merits of this technology are its clean carbon byproduct, fuel flexibility, reduction in CO_x emissions, and comparative simplicity and compactness. The reaction for this mechanism is presented in Equation (26) [87]:



Pyrolysis can be grouped into high (over 800 °C), medium (500–800 °C), and low temperatures (up to 500 °C). Fast pyrolysis (FP) is a process that is used to transform organic material into products with higher energy content. Products of FP appear in all three phases, i.e., liquid, solid, and gas. The possibility for fouling by the formed carbon is one of the challenges associated with this method; however, its proponents are of the view that it can be reduced using the suitable design [88]. Pyrolysis could play a key role in the production of hydrogen, since it has the ability to reduce the emission of carbon monoxide and carbon dioxide and could also be operated in a way that recovers a significant portion of solid carbon [87].

Hydrogen Production through Gasification

Biomass gasification is regarded as a potential way of RE hydrogen production. Biomass gasification is identified as the most economical and efficient way for the production of hydrogen. It is a high temperature partial oxidation process where biomass, which is a solid carbonaceous feedstock, is transformed into a gaseous mixture (CH_4 , CO_2 , H_2 , CO , tar, light hydrocarbons, ash, minor contaminates, and char) using gasifying agents [89]. Biomass gasification's performance is affected by at least 20 operational parameters regarding the feedstock and gasifier, which include the gasifier's geometrical configuration, flow rate, type of gasifying agent, reaction/residence time, pressure and temperature of the gasification, the gasifying agent/biomass ratios, etc. [89,90]. The product distribution and

the composition of gas hinges on several factors, which include the reactor type and the temperature of the gasification. The most vital gasifier types are the entrained flow gasifier and the fixed bed gasifier (updraft or downdraft fixed beds). A significant gas conditioning needs to be included in these gasifiers along with inorganic and tars impurities removal and the subsequent transformation of CO to H₂ through WGS [91].

Biomass gasification normally occurs with a temperature range of 700–1200 °C, using oxygen, air, steam, or their combination as a gasifying agent. Steam enhances the formation of H₂ and generates a high heating value gas without nitrogen. Even though steam gasification has higher energy cost as a result of its highly endothermic nature compared to air gasification, it prevents the need for an expensive oxygen separation process [92,93]. An experimental study [94] indicated that the process of steam gasification that is built based on the fluidized bed reactor with/without added O₂ can produce quantities ranging from 10–16 MJ (Nm³)^{−1} gas H₂ content of 30–60 vol%. This is because there is an absence of nitrogen from air gasification in the products; additionally, there is the possibility of a homogenous WGS during the early stages of the gasification process to increase the production of hydrogen [95]. The production of hydrogen via the biomass steam gasification method is schematically presented in Figure 11.

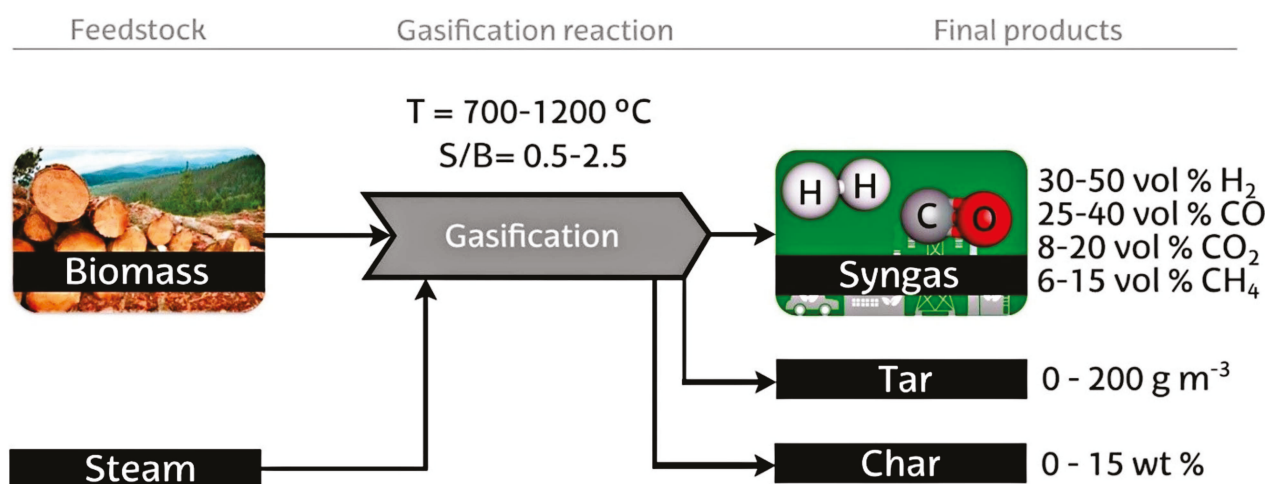


Figure 11. Diagram of the biomass steam gasification procedure for hydrogen production [92]. Reproduced with permission from Elsevier, 2022.

An innovative mechanism to synthesize H₂ without carbon dioxide or carbon monoxide fuel cells via biomass reactions, alkali metal hydroxides as well as water vapor at comparatively low temperatures (473–623 K) under atmospheric pressure was proposed by [96]. The reaction for this proposed method is as presented in Equation (27). Basic reactions for the gasification process for biomass are presented in Table 2.



Table 2. Basic reactions for the gasification process for biomass [97].

Reaction Type	Equation of the Reaction
Pyrolysis	$\text{C}_6\text{H}_{10}\text{O}_5 \rightarrow 5\text{CO} + 5\text{H}_2 + \text{C}$ $\text{C}_6\text{H}_{10}\text{O}_5 \rightarrow 5\text{CO} + 3\text{H}_2 + \text{CH}_4$
Partial oxidation	$\text{C}_6\text{H}_{10}\text{O}_5 + \frac{1}{2}\text{O}_2 \rightarrow 6\text{CO} + 5\text{H}_2$ $\text{C}_6\text{H}_{10}\text{O}_5 + \text{O}_2 \rightarrow 5\text{CO} + 5\text{H}_2 + \text{CO}_2$ $\text{C}_6\text{H}_{10}\text{O}_5 + 2\text{O}_2 \rightarrow 3\text{CO} + 5\text{H}_2 + 3\text{CO}_2$
Steam reforming	$\text{C}_6\text{H}_{10}\text{O}_5 + \text{H}_2\text{O} \rightarrow 6\text{CO} + 6\text{H}_2$ $\text{C}_6\text{H}_{10}\text{O}_5 + 3\text{H}_2\text{O} \rightarrow 4\text{CO} + 2\text{CO}_2 + 8\text{H}_2$ $\text{C}_6\text{H}_{10}\text{O}_5 + 7\text{H}_2\text{O} \rightarrow 6\text{CO}_2 + 12\text{H}_2$

Hydrogen Production via Biomass Combustion

Combustion is basically the burning of any form of fuel to release energy in the form of heat in the presence of air. In this mechanism, biomass burns in a furnace or boiler directly with the presence of excess air, which can be used for steam production and the resultant steam used to drive turbines, compressors, or pumps in any chemical process. Biomass has advantages as a combustion feedstock due to the high reactivity of the resulting char and the fuel, and also the high volatility of the fuel [98]. Biomass combustion is normally not ideal for the production of hydrogen because of the high formation of CO₂ linked to it. The production of hydrogen was 9.56 vol% for algal biomass combustion [99,100]. Several other gases are emitted; some of these are NO_x, SO_x, CO_x, and CH₄, which are all dependent on the composition and source of the biomass. There is a high cost associated with the treatment of these gases, which increases the total cost of the process [99,101].

3.2.3. Hydrogen Production Yield and Some Limitations Associated with the Various Biomass Processes

Despite the hydrogen production potential related to the various biomass methods presented in the earlier section, the various techniques have some limitations which can hinder their use for the generation of hydrogen. Some of these are highlighted below:

- Biological process:
 - **Photo-fermentation**—this mechanism has low yield relative to the production of H₂; it is also required to control the bacteria. Moreover, it requires a high surface area and has a high energy demand. The H₂ yield is estimated to be around 9–49 g/kg feedstock [83,102].
 - **Dark fermentation**—this process requires pre-treatment; additionally, it has a high number of by-products, while the rate of production and yield of H₂ is also low. The H₂ yield is estimated to be around 4–44 g/kg feedstock [103–105].
- Thermochemical process:
 - **Biomass pyrolysis**—this technology requires catalysts regeneration, emission of CO₂, formation of char and tar, and variation in H₂ as a result of complexity in biomass and variation in composition; the cost of reactor is also high. The H₂ yield is estimated to be around 25–65 g/kg feedstock [103,106].
 - **Biomass gasification**—the limitations linked to this process are high operating temperature, variation in H₂ as a result of complexity in biomass and variation in composition, formation of char and tar, which leads to catalyst deactivation, expensive reactor, and that CO₂ emissions and catalyst regeneration are required. The H₂ yield is estimated to be around 40–190 g/kg feedstock [103].
 - **Steam reforming**—this requires catalysts regeneration, operates under high temperatures, and emits CO₂. The H₂ yield is estimated to be around 40–130 g/kg feedstock [64].
 - **Partial oxidation**—this also operates under high temperature, includes CO₂ emission, is adapted for only few molecules, and requires a high amount of oxygen. The H₂ yield is estimated to be around 16–140 g/kg feedstock [107,108].

4. Role of Hydrogen in the World's Future Energy Generation and Decarbonization

Hydrogen energy, as indicated earlier, has the potential to serve as an energy carrier, and this source of energy has become key in relation to global sustainable growth both in developed and developing countries [109]. Research has predicted that the world will require about 600 to 1000 EJ of primary power by 2050 [110]. Energy demands are expected to increase even more in developing countries, where the need for power is high for their development and poverty alleviation [111]. However, the current global primary energy mix is dominated by fossil fuels, which are predicted to be depleted in about 50 years using the current rate of its consumption [72,112]. Fuel cells and hydrogen are mostly seen as important technologies for a sustainable energy supply in the future. It is projected that RS

shares of 36% by 2025 and 69% by 2050 on entire demand for energy could result in an 11% hydrogen shares by 2025 and 34% by 2050 [113]. Hydrogen can be transported and stored; it can be transformed into electrical energy using fuel cells. Hydrogen is ecologically friendly, contingent on the source of energy for its production; in the case of production from water, it returns to water after oxidation. A number of reasons exist as to why hydrogen is an appropriate and logical choice as a chemical fuel for the replacement of fossil fuels. The main reason is that it is a complementary energy carrier to electricity [114].

Maybe the current best-known use of hydrogen is in the transportation sector. Drivers of electric vehicles often complain about the range and time needed for recharging. Fuel cell electric vehicles that operate using hydrogen do not have such concerns, since they possess much longer range, need few behavioral changes, and have a faster refueling time. Heating of homes can also be done using hydrogen. It can be either burned alone or combined with natural gas. Proponents of hydrogen energy have suggested the use of surplus energy from wind farms at night should be harnessed to produce hydrogen, which can be stored in high pressure tanks or caverns for use [115].

The production of hydrogen could help in the reduction of curtailment in grids with a high share of variable RE electricity. Water electrolysis is a well-established industrial technology which uses electricity from the grid. It is expected to play a role on the near-period H_2 market too [113]. It is, however, not likely to generate substantial quantity of hydrogen using wholly inexpensive or free “otherwise curtailed” electricity if, for instance, the operation of electrolyzers is only about 10% of the time or less. Considering this rate of utilization, produced hydrogen may not be competitive even if zero-cost electricity is considered. This could possibly change if the cost of electrolyzer reduces further. In order to decrease the cost of production for hydrogen, the utilization rate of electrolyzers should be higher, which is not compatible with the irregular accessibility of curtailed electricity. There is a need to strike a balance between the buying of electricity at all times of low prices and the increasing of electrolyzers utilization [116].

Hydrogen is seen as a potential source of energy generation that could help lower the emission of CO_2 . A comparison among fossil fuels and hydrogen technologies is shown in Figure 12. It is estimated that the use of hydrogen generated from traditional approaches can minimize the emission of carbon by nearly 20% when used in fuel cells. Therefore, this means that emission of carbon can be significantly reduced through the production of hydrogen using RS [117]. The Hydrogen Council indicated in their report that H_2 demand and supply could reach 10 EJ per year by the close of 2050, which is further projected to increase by approximately 5–10% per year after 2050. Therefore, H_2 can be said to be a potential strong contender in the world’s energy system in the future [118].

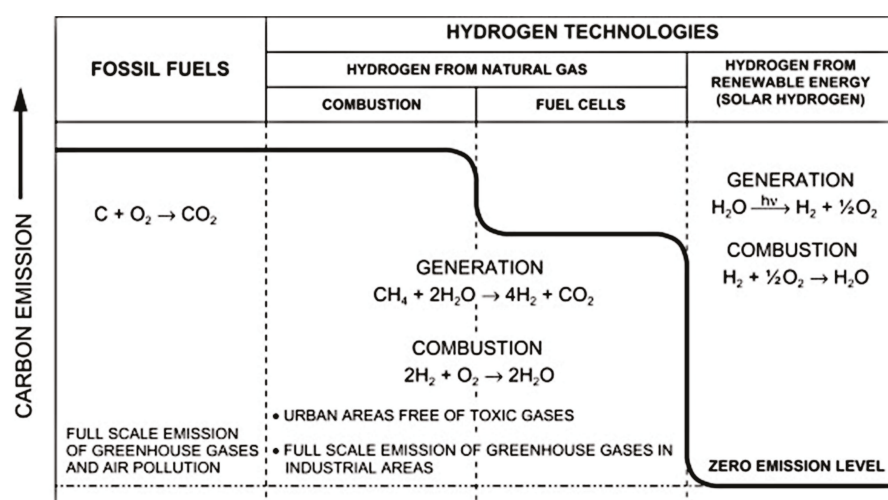


Figure 12. Impact of hydrogen production and combustion on emission of carbon [117]. Reproduced with permission from Elsevier, 2022.

Cost Estimates for the Production of Hydrogen

The cost of obtaining hydrogen can be divided into logistics and production costs. Financial conditions such as cost of capital and local regulations also affect the final cost of hydrogen. At the production stage, the cost of the source of power, i.e., renewable power or fossil fuels, is key to the variable costs and, hence, affect the final competitiveness of every technology [119].

According to the Hydrogen Council, H₂ was significantly used in 2020; it could potentially solve about 8% of the global energy demand (GED) and it has a production cost of about 2.50 \$/kg. The cost of production has been projected to reduce to about 1.80 \$/kg by 2030 to solve the GED by about 15% [120,121]. A summary of recent cost estimates for some selected technologies for the production of hydrogen is provided in Table 3.

Table 3. Selected methods of hydrogen production with their cost and production efficiencies refs. [70,122,123].

Production Mechanism	Cost, \$/kg	Efficiency of Process, %
Electrolysis	10.30	60–80
Thermolysis	7.98–8.40	20–45
Photolysis	8–10	0.06
Dark fermentation	2.57	60–80
Gasification	1.77–2.05	30–40
Photo fermentation	2.83	0.1
Steam reforming	2.27	74–85
Pyrolysis	1.59–1.70	35–50
Indirect bio photolysis	1.42	-
Direct bio photolysis	2.13	-
Solar thermal electrolysis	5.10–10.49	-
Solar thermolysis	7.98–8.40	-
Wind electrolysis	5.89–6.03	-
Photo-electrolysis	10.36	0.06

According to IRENA [124], the use of electricity from RS to generate hydrogen could help make it competitive in terms of cost relative to fossil fuels by 2030. An amalgamation of decreasing costs of wind and solar power, economies of scale for electrolyzers, and improved performance could help in its realization.

5. Challenges to the Scaling-Up of Hydrogen Production

This section presents some identified barriers that are hindering the production of hydrogen. It can be safe to say that the key challenges that are associated with the development of clean hydrogen is not only about the scaling up of the production of hydrogen, but also largely about the shift from carbon-intensive to low-carbon hydrogen production [125]. Some general barriers or challenges that could affect green hydrogen production are discussed below:

- Absence of a value chain for clean hydrogen—absence of existing value chain for clean hydrogen is identified as one of the major barriers in the sector that has to be overcome to help develop a low-carbon hydrogen economy. The value chain for hydrogen is currently dominated by fossil fuels; there are limited projects that focus on low-carbon hydrogen. If clean hydrogen would become globally competitive, it will require the creation of entirely new value chains. The main challenge is in relation to which path to pursue, which is particularly due to the fact that hydrogen can follow several routes

in the area of demand, supply chains, and handling. It is producible, transportable, and distributable in several forms, and different sectors demand it. Therefore, the most viable outcome will rely on the infrastructures and technologies that are involved which may differ in different areas and applications. In relation to the production of hydrogen, the key challenge would be about the selection of the appropriate mechanism for its production, e.g., blue, green, or yellow hydrogen. Whereas all three mechanisms produce the same final outcome, i.e., low-carbon hydrogen, they come with dissimilar implications relative to industry, infrastructure, and most importantly effect on the environment [125].

- Storage and transportation of hydrogen—this continues to be a weak link in the energy systems of hydrogen [126]. A rise in the efficiency of these methods is linked to the resolution of two main matters: hydrogen conversion into a system that has higher density (e.g., liquefaction) and the safety improvement of conveyor systems and tanks. Additionally, while the initial matter has been studied with some hands-on solutions, problems in relation to the safe management of hydrogen has not yet been comprehensively studied [127,128]. The various techniques for storing hydrogen are presented in Figure 13. It groups the various approaches into three: (1) physical storage in liquid or pure gas forms, where there is no physical or chemical bonding with other materials, (2) adsorption, in this case the hydrogen combines with other substances through weak van der Waals bonds, (3) chemical storage, in this case other materials (e.g., chemical and metal hydrides) and the hydrogen forms chemical bonds [129].
- High production cost—the production cost for H_2 is relatively high as a result of its immature technologies, which prevents competition with conventional hydrocarbon resources-based technologies [127]. RE-based hydrogen production mechanisms at present cannot generate hydrogen at a price that is competitive with the hydrocarbons. The high capital expenditure (CAPEX) that is required for RE-based hydrogen production is a major hindrance [130,131]. The low capacity factor for RE systems coupled with the high upfront financial burden renders it unviable with its current technologies [132]. The compression to minimize its volume for transportation bases also increases its cost, since the compression requires an advanced process. Such processes usually need expensive equipment and energy, which inflates the cost of hydrogen. Hydrogen storage in metal hydrides are possible options for their compression. Nevertheless, the metal hydrides are heavy, usually costly, and have limited lifetime, which makes such a process less practical and expensive [39,133].
- Require international standards—it is an emerging market which requires international standards and regulations, which is currently not available, which is a major hinderance to the development of a global market for hydrogen. This has led to a situation where individual countries formulate their own internal regulations and standards. The absence of common standards and regulations hinders the diffusion of hydrogen, which restrains its potentials. Formulating a common international framework is key to prevent unfair competition and free riding [125]. Areas that could gain from common standards and international harmonization include pipeline specifications and hydrogen purity for the industry, safety protocols for the sector, comparable ISO standards in the area of transportation, and guarantees of origin [134].
- Risks in investment—the hydrogen sector has risks in its supply chain as well as uncertainties on its market, which is expected to persist for a while, particularly where there are tight final product margins. Some explicit risks in the sector include creation of a monopoly in hydrogen suppliers of low-carbon hydrogen at high cost, and variations in cross-border environmental regulations. Governments are, therefore, encouraged to participate in financing projects across borders in order to help manage such risks [134].
- Flammability—the dissipation of liquid hydrogen occurs quickly due to its small molecular size, and also because it has a high diffusion coefficient. Therefore, it reduces hydrogen's localized concentration in air and the extent of time for a potential

hazard; the size of combustible cloud, however, increases. Because hydrogen has a very small energy barrier of 0.017 mJ for combustion in air, and a high flammability range of 4–74%, it tends to burn very easily with little source of ignition/spark; moreover, it is very difficult to extinguish such combusting flame [135].

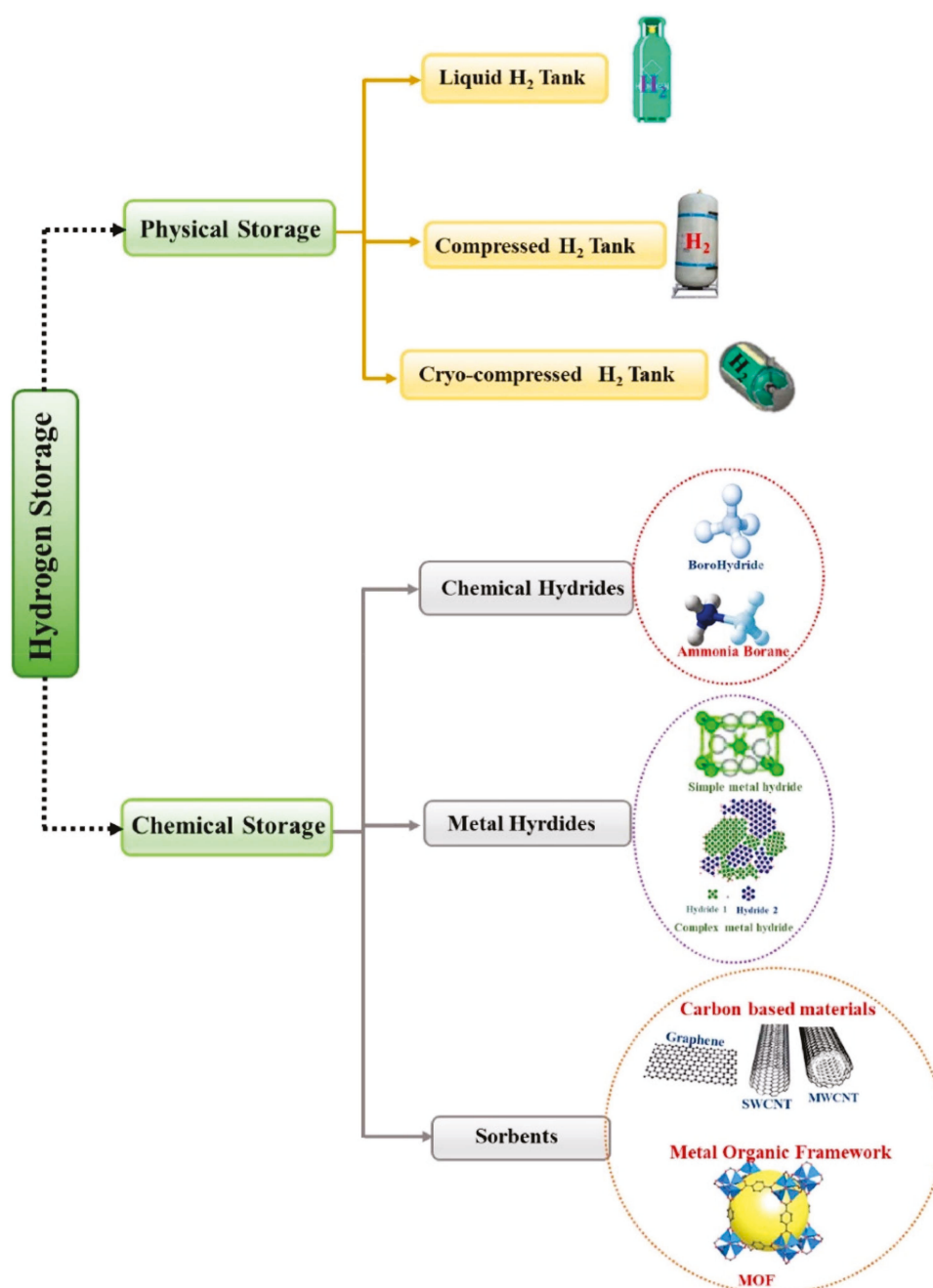


Figure 13. Various mechanisms for hydrogen storage [129]. Reproduced with permission from Elsevier, 2022.

6. Possible Strategies to Scale Up Production

Fossil-based hydrogen production technologies have a well-established feedstock infrastructure, matured production technologies, and they are also more commercialized. The technology for water electrolysis is also well matured and uses existing infrastructure and grid. These technologies are expected to play a key role in the short-term hydrogen supply market. Coal gasification and steam reforming of natural gas with carbon capture

may in the mid-term continue on the hydrogen market along with biomass gasification. In the long term, water electrolysis, which uses RE electricity, thermochemical cycles, photoelectrochemical, and biological methods, is expected to play a major role on the hydrogen market [30]. PEM electrolyzers are nearing maturity technically, and within economies of scale. Several regions, such as Europe, California, and Japan, have started its commercial deployment. The objective is to use existing infrastructure, for instance, gas networks, and get ready for hydrogen production through RE to partially replace fossil fuel-based energy supply [116]. Furthermore, solar technologies' efficiency is comparatively low; therefore, it is important to improve the materials used and also develop catalysis that can help improve the efficiency. Since it is also very important to produce hydrogen with minimum environmental impact, technologies such as photonic water splitting and wind-based electrolysis, which are emerging low-emission technologies, are potential technologies that can also be used in the long term [14].

It is important to institute an appropriate regulatory framework to encourage private sector investments. Such a framework could take into consideration the following [116]:

- Introduction of tariffs on long-term gas grid injection, de-risking instruments to help boost the uptake on the market to support hydrogen deployment and infrastructure, introduction of take-or-pay contracts, and schemes that allow the exemption from electricity levies and grid charges.
- Technology-neutral instruments that aims at the end-user should be adopted, for instance, mandates for RE content in the industrial sector and emission restrictions, which will trigger the demand of hydrogen in a structural manner and rationalize infrastructure investments while addressing issues that relate to carbon leakage. Financial support measures, such as tax rebates and waivers, and subsidies on capital expenditure are required to cover the initial cost premium relative to existing technologies.

7. Conclusions and Future Research Recommendations

Hydrogen is identified as an energy carrier that has the potential to help the world minimize its levels of GHG emissions, which are occasioned by the reliance on fossil fuels for the generation of energy. This study, therefore, presents a comprehensive review of the various technologies available for the production of clean hydrogen, limitations of the various technologies, and challenges that hinders the scaling up of the hydrogen economy. Production of hydrogen through RS offers several advantages, e.g., aside from its clean nature, the potential for a distributed hydrogen supply network model. As presented in this study, apart from the presence of the technical challenges associated with the various technologies, there are also other factors which serve as hinderances to the scaling up of the hydrogen economy. Key among these are issues relating to the absence of a value chain for clean hydrogen, storage and transportation of hydrogen, high cost of production, lack of international standards, risks in investment, and flammability.

Future studies on the various clean technologies for hydrogen should focus on the enhancement of their efficiencies. Technologies such as the use of pulsating electric fields and the use of ultrasonic fields must be researched to help the improvement of the efficiencies of RE hydrogen production. In terms of the membranes for the splitting of water, research should concentrate on polyimides, poly ether ketone, polyethylene, etc., which are economically viable. Other studies can also assess the various options that can be employed to commercialize RE-based hydrogen production; such studies can look at available infrastructure and potential market development. Further research is also required in order to understand the basics and complex stages of biohydrogen in order to help stakeholders implement it on large-scale levels. Governments are also encouraged to participate in financing projects across borders in order to help manage risks in the sector. Additionally, the high-temperature environment for biomass supercritical water gasification incurs corrosion issues and energy consumption; as a result, it is recommended to conduct further studies on the reaction thermodynamics and reaction mechanism to help obtain the optimum method that minimizes them, including the tar formed as a by-product.

Government organizations, researchers, stakeholders, and policymakers are expected to use findings in this study to provide guidelines in shaping the roadmap of the hydrogen sector globally.

Future studies can also review the various materials, reactors, and industrial possibilities of the various technologies to help stakeholders know the research and development trend in the hydrogen sector.

Author Contributions: Conceptualization, E.B.A.; methodology, E.B.A.; validation, E.B.A. and C.N.; formal analysis, E.B.A. and C.N.; investigation, E.B.A.; resources, E.B.A., C.N., S.K. and A.M.A.; data curation, E.B.A.; writing—original draft preparation, E.B.A.; writing—review and editing, E.B.A., C.N., S.K. and A.M.A.; visualization, E.B.A., C.N., S.K. and A.M.A.; project administration, E.B.A.; funding acquisition, E.B.A., S.K. and A.M.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Deputyship for Research & Innovation, Ministry of Education in Saudi Arabia through the project number “IF_2020_NBU_403”.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors extend their appreciation to the Deputyship for Research & Innovation, Ministry of Education in Saudi Arabia for funding this research work through the project number “IF_2020_NBU_403”. The authors gratefully thank the Prince Faisal bin Khalid bin Sultan Research Chair in Renewable Energy Studies and Applications (PFCRE) at Northern Border University for their support and assistance.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviation

AWE	Anion exchange membranes
CAPEX	Capital expenditure
CCUS	Carbon Capture, Utilization, and Storage
DF	Dark fermentation
FP	Fast pyrolysis
GDP	Gross domestic product
GED	Global energy demand
GHG	Greenhouse gases
HER	Hydrogen evolution reaction
RS	Renewable sources
IEA	International Energy Agency
KOH	Potassium hydroxide
SOE	Solid oxide water electrolysis
SMR	Steam methane reforming
OER	Oxygen evolution reaction
PEMs	Proton exchange membranes
PNS	Purple non-sulfur
WGS	Water gas shift
ΔH	Heat of reaction
ΔG	Free energy of the reaction

References

1. Agyekum, E.B. Energy Poverty in Energy Rich Ghana: A SWOT Analytical Approach for the Development of Ghana’s Renewable Energy. *Sustain. Energy Technol. Assess.* **2020**, *40*, 100760. [CrossRef]
2. Agyekum, E.B.; Velkin, V.I. Optimization and Techno-Economic Assessment of Concentrated Solar Power (CSP) in South-Western Africa: A Case Study on Ghana. *Sustain. Energy Technol. Assess.* **2020**, *40*, 100763. [CrossRef]

3. Gyamfi, B.A.; Adebayo, T.S.; Bekun, F.V.; Agyekum, E.B.; Kumar, N.M.; Alhelou, H.H.; Al-Hinai, A. Beyond Environmental Kuznets Curve and Policy Implications to Promote Sustainable Development in Mediterranean. *Energy Rep.* **2021**, *7*, 6119–6129. [CrossRef]
4. Tarhan, C.; Çil, M.A. A Study on Hydrogen, the Clean Energy of the Future: Hydrogen Storage Methods. *J. Energy Storage* **2021**, *40*, 102676. [CrossRef]
5. Zhao, Y.; Ramzan, M.; Adebayo, T.S.; Oladipupo, S.D.; Adeshola, I.; Agyekum, E.B. Role of Renewable Energy Consumption and Technological Innovation to Achieve Carbon Neutrality in Spain: Fresh Insights from Wavelet Coherence and Spectral Causality Approaches. *Front. Environ. Sci.* **2021**, *9*, 769067. [CrossRef]
6. Yaqoob, S.J.; Motahhir, S.; Agyekum, E.B. A New Model for a Photovoltaic Panel Using Proteus Software Tool under Arbitrary Environmental Conditions. *J. Clean. Prod.* **2022**, *333*, 130074. [CrossRef]
7. Adebayo, T.S.; Awosusi, A.A.; Oladipupo, S.D.; Agyekum, E.B.; Jayakumar, A.; Kumar, N.M. Dominance of Fossil Fuels in Japan's National Energy Mix and Implications for Environmental Sustainability. *Int. J. Environ. Res. Public Health* **2021**, *18*, 7347. [CrossRef] [PubMed]
8. Oliveira, A.M.; Beswick, R.R.; Yan, Y. A Green Hydrogen Economy for a Renewable Energy Society. *Curr. Opin. Chem. Eng.* **2021**, *33*, 100701. [CrossRef]
9. Yang, J.; Sudik, A.; Wolverson, C.; Siegel, D.J. High Capacity Hydrogen Storage Materials: Attributes for Automotive Applications and Techniques for Materials Discovery. *Chem. Soc. Rev.* **2010**, *39*, 656–675. [CrossRef]
10. Da Silva Veras, T.; Mozer, T.S.; da Costa Rubim Messeder dos Santos, D.; da Silva César, A. Hydrogen: Trends, Production and Characterization of the Main Process Worldwide. *Int. J. Hydrogen Energy* **2017**, *42*, 2018–2033. [CrossRef]
11. Hanley, E.S.; Deane, J.; Gallachóir, B.Ó. The Role of Hydrogen in Low Carbon Energy Futures—A Review of Existing Perspectives. *Renew. Sustain. Energy Rev.* **2018**, *82*, 3027–3045. [CrossRef]
12. Niaz, S.; Manzoor, T.; Pandith, A.H. Hydrogen Storage: Materials, Methods and Perspectives. *Renew. Sustain. Energy Rev.* **2015**, *50*, 457–469. [CrossRef]
13. Bakenne, A.; Nuttall, W.; Kazantzis, N. Sankey-Diagram-Based Insights into the Hydrogen Economy of Today. *Int. J. Hydrogen Energy* **2016**, *41*, 7744–7753. [CrossRef]
14. Safari, F.; Dincer, I. A Review and Comparative Evaluation of Thermochemical Water Splitting Cycles for Hydrogen Production. *Energy Convers. Manag.* **2020**, *205*, 112182. [CrossRef]
15. Yue, M.; Lambert, H.; Pahon, E.; Roche, R.; Jemei, S.; Hissel, D. Hydrogen Energy Systems: A Critical Review of Technologies, Applications, Trends and Challenges. *Renew. Sustain. Energy Rev.* **2021**, *146*, 111180. [CrossRef]
16. Dawood, F.; Anda, M.; Shafiullah, G.M. Hydrogen Production for Energy: An Overview. *Int. J. Hydrogen Energy* **2020**, *45*, 3847–3869. [CrossRef]
17. Najjar, Y.S. Hydrogen Safety: The Road toward Green Technology. *Int. J. Hydrogen Energy* **2013**, *38*, 10716–10728. [CrossRef]
18. Parra, D.; Valverde, L.; Pino, F.J.; Patel, M.K. A Review on the Role, Cost and Value of Hydrogen Energy Systems for Deep Decarbonisation. *Renew. Sustain. Energy Rev.* **2019**, *101*, 279–294. [CrossRef]
19. Kovač, A.; Paranos, M.; Marciuš, D. Hydrogen in Energy Transition: A Review. *Int. J. Hydrogen Energy* **2021**, *46*, 10016–10035. [CrossRef]
20. Maggio, G.; Nicita, A.; Squadrito, G. How the Hydrogen Production from RES Could Change Energy and Fuel Markets: A Review of Recent Literature. *Int. J. Hydrogen Energy* **2019**, *44*, 11371–11384. [CrossRef]
21. Abe, J.O.; Popoola, A.P.I.; Ajenifuja, E.; Popoola, O.M. Hydrogen Energy, Economy and Storage: Review and Recommendation. *Int. J. Hydrogen Energy* **2019**, *44*, 15072–15086. [CrossRef]
22. Liu, W.; Sun, L.; Li, Z.; Fujii, M.; Geng, Y.; Dong, L.; Fujita, T. Trends and Future Challenges in Hydrogen Production and Storage Research. *Env. Sci. Pollut. Res.* **2020**, *27*, 31092–31104. [CrossRef] [PubMed]
23. Ji, M.; Wang, J. Review and Comparison of Various Hydrogen Production Methods Based on Costs and Life Cycle Impact Assessment Indicators. *Int. J. Hydrogen Energy* **2021**, *46*, 38612–38635. [CrossRef]
24. Hosseini, S.E.; Wahid, M.A. Hydrogen Production from Renewable and Sustainable Energy Resources: Promising Green Energy Carrier for Clean Development. *Renew. Sustain. Energy Rev.* **2016**, *57*, 850–866. [CrossRef]
25. El-Emam, R.S.; Özcan, H. Comprehensive Review on the Techno-Economics of Sustainable Large-Scale Clean Hydrogen Production. *J. Clean. Prod.* **2019**, *220*, 593–609. [CrossRef]
26. Okonkwo, E.C.; Al-Breiki, M.; Bicer, Y.; Al-Ansari, T. Sustainable Hydrogen Roadmap: A Holistic Review and Decision-Making Methodology for Production, Utilisation and Exportation Using Qatar as a Case Study. *Int. J. Hydrogen Energy* **2021**, *46*, 35525–35549. [CrossRef]
27. Lane, B.; Reed, J.; Shaffer, B.; Samuelsen, S. Forecasting Renewable Hydrogen Production Technology Shares under Cost Uncertainty. *Int. J. Hydrogen Energy* **2021**, *46*, 27293–27306. [CrossRef]
28. Nikolaidis, P.; Poullikkas, A. A Comparative Overview of Hydrogen Production Processes. *Renew. Sustain. Energy Rev.* **2017**, *67*, 597–611. [CrossRef]
29. Preuster, P.; Alekseev, A.; Wasserscheid, P. Hydrogen Storage Technologies for Future Energy Systems. *Annu. Rev. Chem. Biomol. Eng.* **2017**, *8*, 445–471. [CrossRef]
30. Baykara, S.Z. Hydrogen: A Brief Overview on Its Sources, Production and Environmental Impact. *Int. J. Hydrogen Energy* **2018**, *43*, 10605–10614. [CrossRef]

31. Çelik, D.; Yıldız, M. Investigation of Hydrogen Production Methods in Accordance with Green Chemistry Principles. *Int. J. Hydrogen Energy* **2017**, *42*, 23395–23401. [CrossRef]
32. IEA Hydrogen—Analysis. Available online: <https://www.iea.org/reports/hydrogen> (accessed on 24 November 2021).
33. Wang, M.; Wang, G.; Sun, Z.; Zhang, Y.; Xu, D. Review of Renewable Energy-Based Hydrogen Production Processes for Sustainable Energy Innovation. *Glob. Energy Interconnect.* **2019**, *2*, 436–443. [CrossRef]
34. Zhang, B.; Zhang, S.-X.; Yao, R.; Wu, Y.-H.; Qiu, J.-S. Progress and Prospects of Hydrogen Production: Opportunities and Challenges. *J. Electron. Sci. Technol.* **2021**, *19*, 100080. [CrossRef]
35. Kannah, R.Y.; Kavitha, S.; Karthikeyan, O.P.; Kumar, G.; Dai-Viet, N.V.; Rajesh Banu, J. Techno-Economic Assessment of Various Hydrogen Production Methods—A Review. *Bioresour. Technol.* **2021**, *319*, 124175. [CrossRef] [PubMed]
36. Bradford, M.C.; Konduru, M.V.; Fuentes, D.X. Preparation, Characterization and Application of Cr₂O₃/ZnO Catalysts for Methanol Synthesis. *Fuel Processing Technol.* **2003**, *83*, 11–25. [CrossRef]
37. Hydrogen Council; McKinsey & Company Hydrogen-Insights 2021 Report. Available online: <https://hydrogencouncil.com/wp-content/uploads/2021/02/Hydrogen-Insights-2021-Report.pdf> (accessed on 24 November 2021).
38. Hou, K.; Hughes, R. The Kinetics of Methane Steam Reforming over a Ni/ α -Al₂O Catalyst. *Chem. Eng. J.* **2001**, *82*, 311–328. [CrossRef]
39. Liao, C.-H.; Huang, C.-W.; Wu, J.C.S. Hydrogen Production from Semiconductor-Based Photocatalysis via Water Splitting. *Catalysts* **2012**, *2*, 490–516. [CrossRef]
40. Agyekum, E.B.; Kumar, N.M.; Mehmood, U.; Panjwani, M.K.; Haes Alhelou, H.; Adebayo, T.S.; Al-Hinai, A. Decarbonize Russia—A Best–Worst Method Approach for Assessing the Renewable Energy Potentials, Opportunities and Challenges. *Energy Rep.* **2021**, *7*, 4498–4515. [CrossRef]
41. Nowotny, J.; Sorrell, C.C.; Sheppard, L.R.; Bak, T. Solar-Hydrogen: Environmentally Safe Fuel for the Future. *Int. J. Hydrogen Energy* **2005**, *30*, 521–544. [CrossRef]
42. Malerød-Fjeld, H.; Clark, D.; Yuste-Tirados, I.; Zanón, R.; Catalán-Martinez, D.; Beeaff, D.; Morejudo, S.H.; Vestre, P.K.; Norby, T.; Haugrud, R.; et al. Thermo-Electrochemical Production of Compressed Hydrogen from Methane with Near-Zero Energy Loss. *Nat. Energy* **2017**, *2*, 923–931. [CrossRef]
43. Okonkwo, P.C.; Bhowmik, H.; Mansir, I.B.; Al, M.A.A.A.S.; Al Sfarini, N.F.A. Effect of Electrode Spacing on Hydrogen Production Using a Home-Made Alkaline Electrolyzer. *Mater. Lett.* **2022**, *306*, 130841. [CrossRef]
44. Salari, A.; Hakkaki-Fard, A.; Jalalidil, A. Hydrogen Production Performance of a Photovoltaic Thermal System Coupled with a Proton Exchange Membrane Electrolysis Cell. *Int. J. Hydrogen Energy* **2021**, *47*, 4472–4488. [CrossRef]
45. Ishaq, H.; Dincer, I. Multi-Objective Optimization and Analysis of a Solar Energy Driven Steam and Autothermal Combined Reforming System with Natural Gas. *J. Nat. Gas Sci. Eng.* **2019**, *69*, 102927. [CrossRef]
46. Lu, C.; Li, W.; Zhang, Q.; Liu, L.; Zhang, N.; Qu, B.; Yang, X.; Xu, R.; Chen, J.; Sun, Y. Enhancing Photo-Fermentation Biohydrogen Production by Strengthening the Beneficial Metabolic Products with Catalysts. *J. Clean. Prod.* **2021**, *317*, 128437. [CrossRef]
47. Oh, S.; Nam, W.; Joo, H.; Sarp, S.; Cho, J.; Lee, C.-H.; Yoon, J. Photoelectrochemical Hydrogen Production with Concentrated Natural Seawater Produced by Membrane Process. *Sol. Energy* **2011**, *85*, 2256–2263. [CrossRef]
48. Wang, Y.; Jing, Y.; Lu, C.; Kongjan, P.; Wang, J.; Awasthi, M.K.; Tahir, N.; Zhang, Q. A Syntrophic Co-Fermentation Model for Bio-Hydrogen Production. *J. Clean. Prod.* **2021**, *317*, 128288. [CrossRef]
49. Qiu, Z.; Martín-Yerga, D.; Lindén, P.A.; Henriksson, G.; Cornell, A. Green Hydrogen Production via Electrochemical Conversion of Components from Alkaline Carbohydrate Degradation. *Int. J. Hydrogen Energy* **2021**, *47*, 3644–3654. [CrossRef]
50. Kamaroddin, M.F.A.; Sabli, N.; Nia, P.M.; Abdullah, T.A.T.; Abdullah, L.C.; Izhar, S.; Ripin, A.; Ahmad, A. Phosphoric Acid Doped Composite Proton Exchange Membrane for Hydrogen Production in Medium-Temperature Copper Chloride Electrolysis. *Int. J. Hydrogen Energy* **2020**, *45*, 22209–22222. [CrossRef]
51. Chi, J.; Yu, H. Water Electrolysis Based on Renewable Energy for Hydrogen Production. *Chin. J. Catal.* **2018**, *39*, 390–394. [CrossRef]
52. Ursua, A.; Gandia, L.M.; Sanchis, P. Hydrogen Production From Water Electrolysis: Current Status and Future Trends. *Proc. IEEE* **2012**, *100*, 410–426. [CrossRef]
53. Li, C.; Baek, J.-B. The Promise of Hydrogen Production from Alkaline Anion Exchange Membrane Electrolyzers. *Nano Energy* **2021**, *87*, 106162. [CrossRef]
54. Appleby, A.J.; Crepy, G.; Jacquelin, J. High Efficiency Water Electrolysis in Alkaline Solution. *Int. J. Hydrogen Energy* **1978**, *3*, 21–37. [CrossRef]
55. Diaz, L.A.; Hnát, J.; Heredia, N.; Bruno, M.M.; Viva, F.A.; Paidar, M.; Corti, H.R.; Bouzek, K.; Abuin, G.C. Alkali Doped Poly (2,5-Benzimidazole) Membrane for Alkaline Water Electrolysis: Characterization and Performance. *J. Power Sources* **2016**, *312*, 128–136. [CrossRef]
56. Vincent, I.; Bessarabov, D. Low Cost Hydrogen Production by Anion Exchange Membrane Electrolysis: A Review. *Renew. Sustain. Energy Rev.* **2018**, *81*, 1690–1704. [CrossRef]
57. Koumi Ngoh, S.; Njomo, D. An Overview of Hydrogen Gas Production from Solar Energy. *Renew. Sustain. Energy Rev.* **2012**, *16*, 6782–6792. [CrossRef]
58. Ahmad Kamaroddin, M.F.; Sabli, N.; Tuan Abdullah, T.A.; Siajam, S.I.; Abdullah, L.C.; Abdul Jalil, A.; Ahmad, A. Membrane-Based Electrolysis for Hydrogen Production: A Review. *Membranes* **2021**, *11*, 810. [CrossRef] [PubMed]

59. Ying, Y.P.; Kamarudin, S.K.; Masdar, M.S. Silica-Related Membranes in Fuel Cell Applications: An Overview. *Int. J. Hydrogen Energy* **2018**, *43*, 16068–16084. [CrossRef]
60. Kim, D.J.; Choi, D.H.; Park, C.H.; Nam, S.Y. Characterization of the Sulfonated PEEK/Sulfonated Nanoparticles Composite Membrane for the Fuel Cell Application. *Int. J. Hydrogen Energy* **2016**, *41*, 5793–5802. [CrossRef]
61. Holladay, J.D.; Hu, J.; King, D.L.; Wang, Y. An Overview of Hydrogen Production Technologies. *Catal. Today* **2009**, *139*, 244–260. [CrossRef]
62. Zhou, Z.; Zhlobko, O.; Wu, X.-F.; Aulich, T.; Thakare, J.; Hurley, J. Polybenzimidazole-Based Polymer Electrolyte Membranes for High-Temperature Fuel Cells: Current Status and Prospects. *Energies* **2021**, *14*, 135. [CrossRef]
63. Leng, Y.; Chen, G.; Mendoza, A.J.; Tighe, T.B.; Hickner, M.A.; Wang, C.-Y. Solid-State Water Electrolysis with an Alkaline Membrane. *J. Am. Chem. Soc.* **2012**, *134*, 9054–9057. [CrossRef]
64. Dincer, I.; Acar, C. Review and Evaluation of Hydrogen Production Methods for Better Sustainability. *Int. J. Hydrogen Energy* **2015**, *40*, 11094–11111. [CrossRef]
65. Martinez-Burgos, W.J.; de Souza Candeo, E.; Pedroni Medeiros, A.B.; Cesar de Carvalho, J.; de Andrade Tanobe, V.O.; Soccol, C.R.; Sydney, E.B. Hydrogen: Current Advances and Patented Technologies of Its Renewable Production. *J. Clean. Prod.* **2021**, *286*, 124970. [CrossRef]
66. Kasai, P.H.; Bishop, R.J., Jr. Thermolysis of Water in Contact with Zeolite Masses. U.S. Patent 3,963,830, 16 June 1976.
67. Hsu, K.-T. Cold Chemical Water-Splitting Hydrogen Generation System. U.S. Patent Application 11/188,994, 25 January 2007.
68. Kothari, R.; Buddhi, D.; Sawhney, R.L. Comparison of Environmental and Economic Aspects of Various Hydrogen Production Methods. *Renew. Sustain. Energy Rev.* **2008**, *12*, 553–563. [CrossRef]
69. Furatian, L.; Mohseni, M. Temperature Dependence of 185 nm Photochemical Water Treatment—The Photolysis of Water. *J. Photochem. Photobiol. A Chem.* **2018**, *356*, 364–369. [CrossRef]
70. Kumar, S.S.; Himabindu, V. Hydrogen Production by PEM Water Electrolysis—A Review. *Mater. Sci. Energy Technol.* **2019**, *2*, 442–454.
71. Flamos, A.; Georgallis, P.G.; Doukas, H.; Psarras, J. Using Biomass to Achieve European Union Energy Targets—A Review of Biomass Status, Potential, and Supporting Policies. *Int. J. Green Energy* **2011**, *8*, 411–428. [CrossRef]
72. Pal, D.B.; Singh, A.; Bhatnagar, A. A Review on Biomass Based Hydrogen Production Technologies. *Int. J. Hydrogen Energy* **2021**, *47*, 1461–1480. [CrossRef]
73. Vasilakos, N.P.; Austgen, D.M. Hydrogen-Donor Solvents in Biomass Liquefaction. *Ind. Eng. Chem. Proc. Des. Dev.* **1985**, *24*, 304–311. [CrossRef]
74. Isa, K.M.; Abdullah, T.A.T.; Ali, U.F.M. Hydrogen Donor Solvents in Liquefaction of Biomass: A Review. *Renew. Sustain. Energy Rev.* **2018**, *81*, 1259–1268. [CrossRef]
75. Manish, S.; Banerjee, R. Comparison of Biohydrogen Production Processes. *Int. J. Hydrogen Energy* **2008**, *33*, 279–286. [CrossRef]
76. Łukajtis, R.; Hołowacz, I.; Kucharska, K.; Glinka, M.; Rybarczyk, P.; Przyjazny, A.; Kamiński, M. Hydrogen Production from Biomass Using Dark Fermentation. *Renew. Sustain. Energy Rev.* **2018**, *91*, 665–694. [CrossRef]
77. Adessi, A.; De Philippis, R. Hydrogen Production: Photofermentation. In *Microbial Technologies in Advanced Biofuels Production*; Hallenbeck, P.C., Ed.; Springer: Boston, MA, USA, 2012; pp. 53–75. ISBN 978-1-4614-1208-3.
78. Keskin, T.; Abo-Hashesh, M.; Hallenbeck, P.C. Photofermentative Hydrogen Production from Wastes. *Bioresour. Technol.* **2011**, *102*, 8557–8568. [CrossRef]
79. Mishra, P.; Krishnan, S.; Rana, S.; Singh, L.; Sakinah, M.; Ab Wahid, Z. Outlook of Fermentative Hydrogen Production Techniques: An Overview of Dark, Photo and Integrated Dark-Photo Fermentative Approach to Biomass. *Energy Strategy Rev.* **2019**, *24*, 27–37. [CrossRef]
80. Das, D.; Veziroğlu, T.N. Hydrogen Production by Biological Processes: A Survey of Literature. *Int. J. Hydrogen Energy* **2001**, *26*, 13–28. [CrossRef]
81. Hallenbeck, P.C.; Lazaro, C.Z.; Sagır, E. 3.10—Biohydrogen☆. In *Comprehensive Biotechnology*, 3rd ed.; Moo-Young, M., Ed.; Pergamon: Oxford, UK, 2019; pp. 128–139, ISBN 978-0-444-64047-5.
82. Aydin, M.I.; Karaca, A.E.; Qureshy, A.M.M.I.; Dincer, I. A Comparative Review on Clean Hydrogen Production from Wastewaters. *J. Environ. Manag.* **2021**, *279*, 111793. [CrossRef]
83. Ni, M.; Leung, D.Y.C.; Leung, M.K.H.; Sumathy, K. An Overview of Hydrogen Production from Biomass. *Fuel Processing Technol.* **2006**, *87*, 461–472. [CrossRef]
84. Antal, T.K.; Lindblad, P. Production of H₂ by Sulphur-Deprived Cells of the Unicellular Cyanobacteria *Gloeocapsa alpicola* and *Synechocystis* sp. PCC 6803 during Dark Incubation with Methane or at Various Extracellular PH. *J. Appl. Microbiol.* **2005**, *98*, 114–120. [CrossRef]
85. Fremaux, S.; Beheshti, S.-M.; Ghassemi, H.; Shahsavan-Markadeh, R. An Experimental Study on Hydrogen-Rich Gas Production via Steam Gasification of Biomass in a Research-Scale Fluidized Bed. *Energy Convers. Manag.* **2015**, *91*, 427–432. [CrossRef]
86. Muradov, N. Emission-Free Fuel Reformers for Mobile and Portable Fuel Cell Applications. *J. Power Sources* **2003**, *118*, 320–324. [CrossRef]
87. Kalamaras, C.M.; Efstathiou, A.M. Hydrogen Production Technologies: Current State and Future Developments. In *Proceedings of the Conference Papers in Science*; Hindawi: London, UK, 2013; Volume 2013.

88. Bičáková, O.; Straka, P. Production of Hydrogen from Renewable Resources and Its Effectiveness. *Int. J. Hydrogen Energy* **2012**, *37*, 11563–11578. [CrossRef]
89. Ahmed, T.Y.; Ahmad, M.M.; Yusup, S.; Inayat, A.; Khan, Z. Mathematical and Computational Approaches for Design of Biomass Gasification for Hydrogen Production: A Review. *Renew. Sustain. Energy Rev.* **2012**, *16*, 2304–2315. [CrossRef]
90. Chen, G.; Andries, J.; Luo, Z.; Spliethoff, H. Biomass Pyrolysis/Gasification for Product Gas Production: The Overall Investigation of Parametric Effects. *Energy Convers. Manag.* **2003**, *44*, 1875–1884. [CrossRef]
91. Kirtay, E. Recent Advances in Production of Hydrogen from Biomass. *Energy Convers. Manag.* **2011**, *52*, 1778–1789. [CrossRef]
92. Arregi, A.; Amutio, M.; Lopez, G.; Bilbao, J.; Olazar, M. Evaluation of Thermochemical Routes for Hydrogen Production from Biomass: A Review. *Energy Convers. Manag.* **2018**, *165*, 696–719. [CrossRef]
93. Parthasarathy, P.; Narayanan, K.S. Hydrogen Production from Steam Gasification of Biomass: Influence of Process Parameters on Hydrogen Yield—A Review. *Renew. Energy* **2014**, *66*, 570–579. [CrossRef]
94. Turn, S.; Kinoshita, C.; Zhang, Z.; Ishimura, D.; Zhou, J. An Experimental Investigation of Hydrogen Production from Biomass Gasification. *Int. J. Hydrogen Energy* **1998**, *23*, 641–648. [CrossRef]
95. Dou, B.; Zhang, H.; Song, Y.; Zhao, L.; Jiang, B.; He, M.; Ruan, C.; Chen, H.; Xu, Y. Hydrogen Production from the Thermochemical Conversion of Biomass: Issues and Challenges. *Sustain. Energy Fuels* **2019**, *3*, 314–342. [CrossRef]
96. Ishida, M.; Takenaka, S.; Yamanaka, I.; Otsuka, K. Production of CO X-Free Hydrogen from Biomass and NaOH Mixture: Effect of Catalysts. *Energy Fuels* **2006**, *20*, 748–753. [CrossRef]
97. El-Shafie, M.; Kambara, S.; Hayakawa, Y. Hydrogen Production Technologies Overview. *JPEE* **2019**, *7*, 107–154. [CrossRef]
98. Demirbas, A. Potential Applications of Renewable Energy Sources, Biomass Combustion Problems in Boiler Power Systems and Combustion Related Environmental Issues. *Prog. Energy Combust. Sci.* **2005**, *31*, 171–192. [CrossRef]
99. Shahbaz, M.; Al-Ansari, T.; Aslam, M.; Khan, Z.; Inayat, A.; Athar, M.; Naqvi, S.R.; Ahmed, M.A.; McKay, G. A State of the Art Review on Biomass Processing and Conversion Technologies to Produce Hydrogen and Its Recovery via Membrane Separation. *Int. J. Hydrogen Energy* **2020**, *45*, 15166–15195. [CrossRef]
100. Ripoll, N.; Silvestre, C.; Paredes, E.; Toledo, M. Hydrogen Production from Algae Biomass in Rich Natural Gas-Air Filtration Combustion. *Int. J. Hydrogen Energy* **2017**, *42*, 5513–5522. [CrossRef]
101. Saidur, R.; Ahamed, J.U.; Masjuki, H.H. Energy, Exergy and Economic Analysis of Industrial Boilers. *Energy Policy* **2010**, *38*, 2188–2197. [CrossRef]
102. Sagir, E.; Ozgur, E.; Gunduz, U.; Eroglu, I.; Yucel, M. Single-Stage Photofermentative Biohydrogen Production from Sugar Beet Molasses by Different Purple Non-Sulfur Bacteria. *Bioprocess Biosyst. Eng.* **2017**, *40*, 1589–1601. [CrossRef] [PubMed]
103. Lepage, T.; Kammoun, M.; Schmetz, Q.; Richel, A. Biomass-to-Hydrogen: A Review of Main Routes Production, Processes Evaluation and Techno-Economical Assessment. *Biomass Bioenergy* **2021**, *144*, 105920. [CrossRef]
104. Wang, J.; Yin, Y. Fermentative Hydrogen Production Using Pretreated Microalgal Biomass as Feedstock. *Microb. Cell Factories* **2018**, *17*, 22. [CrossRef]
105. Kaparaju, P.; Serrano, M.; Thomsen, A.B.; Kongjan, P.; Angelidaki, I. Bioethanol, Biohydrogen and Biogas Production from Wheat Straw in a Biorefinery Concept. *Bioresour. Technol.* **2009**, *100*, 2562–2568. [CrossRef]
106. Zhao, B.; Zhang, X.; Sun, L.; Meng, G.; Chen, L.; Xiaolu, Y. Hydrogen Production from Biomass Combining Pyrolysis and the Secondary Decomposition. *Int. J. Hydrogen Energy* **2010**, *35*, 2606–2611. [CrossRef]
107. Wang, Y.; Wang, S.; Zhao, G.; Guo, Y.; Guo, Y. Hydrogen Production by Partial Oxidation Gasification of a Phenol, Naphthalene, and Acetic Acid Mixture in Supercritical Water. *Int. J. Hydrogen Energy* **2016**, *41*, 2238–2246. [CrossRef]
108. Guan, Q.; Wei, C.; Chai, X.; Ning, P.; Tian, S.; Gu, J.; Chen, Q.; Miao, R. Energetic Analysis of Gasification of Biomass by Partial Oxidation in Supercritical Water. *Chin. J. Chem. Eng.* **2015**, *23*, 205–212. [CrossRef]
109. Marechal, F.; Favrat, D.; Jochem, E. Energy in the Perspective of the Sustainable Development: The 2000W Society Challenge. *Resour. Conserv. Recycl.* **2005**, *44*, 245–262. [CrossRef]
110. Smeets, E.M.W.; Faaij, A.P.C.; Lewandowski, I.M.; Turkenburg, W.C. A Bottom-Up Assessment and Review of Global Bio-Energy Potentials to 2050. *Prog. Energy Combust. Sci.* **2007**, *33*, 56–106. [CrossRef]
111. Agyekum, E.B.; Amjad, F.; Mohsin, M.; Ansah, M.N.S. A Bird's Eye View of Ghana's Renewable Energy Sector Environment: A Multi-Criteria Decision-Making Approach. *Util. Policy* **2021**, *70*, 101219. [CrossRef]
112. Hasnaoui, S.; Pauss, A.; Abdi, N.; Grib, H.; Mameri, N. Enhancement of Bio-Hydrogen Generation by Spirulina via an Electrochemical Photo-Bioreactor (EPBR). *Int. J. Hydrogen Energy* **2020**, *45*, 6231–6242. [CrossRef]
113. Balat, H.; Kirtay, E. Hydrogen from Biomass—Present Scenario and Future Prospects. *Int. J. Hydrogen Energy* **2010**, *35*, 7416–7426. [CrossRef]
114. Rosen, M.A.; Koochi-Fayegh, S. The Prospects for Hydrogen as an Energy Carrier: An Overview of Hydrogen Energy and Hydrogen Energy Systems. *Energy Ecol. Environ.* **2016**, *1*, 10–29. [CrossRef]
115. Why Hydrogen Could Be the Future of Green Energy. Available online: <https://www.weforum.org/agenda/2018/05/this-forgotten-element-could-be-the-key-to-our-green-energy-future-heres-why/> (accessed on 16 December 2021).
116. IRENA Hydrogen from Renewable Power: Technology Outlook for the Energy Transition. Available online: <https://www.irena.org/publications/2018/sep/hydrogen-from-renewable-power> (accessed on 17 December 2021).
117. Nowotny, J.; Veziroglu, T.N. Impact of Hydrogen on the Environment. *Int. J. Hydrogen Energy* **2011**, *36*, 13218–13224. [CrossRef]

118. Hydrogen Council. *Hydrogen Council Hydrogen Scaling Up: A Sustainable Pathway for the Global Energy Transition*; Hydrogen Council: Brussels, Belgium, 2017.
119. IRENA. *Hydrogen: A Renewable Energy Perspective*; IRENA: Abu Dhab, United Arab Emirates, 2019; p. 52.
120. Hydrogen Council. *Hydrogen Council Path to Hydrogen Competitiveness: A Cost Perspective*; Hydrogen Council: Brussels, Belgium, 2020.
121. Sharma, S.; Agarwal, S.; Jain, A. Significance of Hydrogen as Economic and Environmentally Friendly Fuel. *Energies* **2021**, *14*, 7389. [CrossRef]
122. Abdalla, A.M.; Hossain, S.; Nisfindy, O.B.; Azad, A.T.; Dawood, M.; Azad, A.K. Hydrogen Production, Storage, Transportation and Key Challenges with Applications: A Review. *Energy Convers. Manag.* **2018**, *165*, 602–627. [CrossRef]
123. Acar, C.; Dincer, I. Hydrogen Production. In *Comprehensive Energy Systems*; Dincer, I., Ed.; Elsevier: Oxford, UK, 2018; pp. 1–40, ISBN 978-0-12-814925-6.
124. IRENA Making Green Hydrogen a Cost-Competitive Climate Solution. Available online: <https://www.irena.org/newsroom/pressreleases/2020/Dec/Making-Green-Hydrogen-a-Cost-Competitive-Climate-Solution> (accessed on 19 December 2021).
125. Scita, R.; Raimondi, P.P.; Noussan, M. *Barriers to the Implementation of a Clean Hydrogen Economy*; Green Hydrogen: Kolding, Denmark; Fondazione Eni Enrico Mattei (FEEM): Milan, MI, USA, 2020; pp. 8–15.
126. Ma, J.; Liu, S.; Zhou, W.; Pan, X. Comparison of Hydrogen Transportation Methods for Hydrogen Refueling Station. *J. Tongji Univ. Nat. Sci.* **2008**, *36*, 615–619.
127. Litvinenko, V. The Role of Hydrocarbons in the Global Energy Agenda: The Focus on Liquefied Natural Gas. *Resources* **2020**, *9*, 59. [CrossRef]
128. Litvinenko, V.S.; Tsvetkov, P.S.; Dvoynikov, M.V.; Buslaev, G.V. Barriers to Implementation of Hydrogen Initiatives in the Context of Global Energy Sustainable Development. *Записки Горного Института* **2020**, *244*, 428–438.
129. Olabi, A.; Bahri, A.S.; Abdelghafar, A.A.; Baroutaji, A.; Sayed, E.T.; Alami, A.H.; Rezk, H.; Abdelkareem, M.A. Large-scale hydrogen production and storage technologies: Current status and future directions. *Int. J. Hydrogen Energy* **2021**, *46*, 23498–23528. [CrossRef]
130. Al-Qahtani, A.; Parkinson, B.; Hellgardt, K.; Shah, N.; Guillen-Gosalbez, G. Uncovering the True Cost of Hydrogen Production Routes Using Life Cycle Monetisation. *Appl. Energy* **2021**, *281*, 115958. [CrossRef]
131. Parkinson, B.; Balcombe, P.; Speirs, J.F.; Hawkes, A.D.; Hellgardt, K. Levelized Cost of CO₂ Mitigation from Hydrogen Production Routes. *Energy Environ. Sci.* **2019**, *12*, 19–40. [CrossRef]
132. Esposito, D.V. Membraneless Electrolyzers for Low-Cost Hydrogen Production in a Renewable Energy Future. *Joule* **2017**, *1*, 651–658. [CrossRef]
133. Midilli, A.; Ay, M.; Dincer, I.; Rosen, M.A. On Hydrogen and Hydrogen Energy Strategies: I: Current Status and Needs. *Renew. Sustain. Energy Rev.* **2005**, *9*, 255–271. [CrossRef]
134. IEA. *The Future of Hydrogen: Seizing Today's Opportunities*; IEA: Paris, France, 2019; p. 203.
135. Ratnakar, R.R.; Gupta, N.; Zhang, K.; van Doorne, C.; Fesmire, J.; Dindoruk, B.; Balakotaiah, V. Hydrogen Supply Chain and Challenges in Large-Scale LH₂ Storage and Transportation. *Int. J. Hydrogen Energy* **2021**, *46*, 24149–24168. [CrossRef]

MDPI AG
Grosspeteranlage 5
4052 Basel
Switzerland
Tel.: +41 61 683 77 34

Membranes Editorial Office
E-mail: membranes@mdpi.com
www.mdpi.com/journal/membranes



Disclaimer/Publisher's Note: The title and front matter of this reprint are at the discretion of the Guest Editor. The publisher is not responsible for their content or any associated concerns. The statements, opinions and data contained in all individual articles are solely those of the individual Editor and contributors and not of MDPI. MDPI disclaims responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.



Academic Open
Access Publishing

mdpi.com

ISBN 978-3-7258-8648-7