Abstract: In this study, by adding zirconium anhydride (ZrO$_2$) particles to a solution of N-methylmorphorline-N-oxide (NMMO) and bamboo cellulose (BC), we used interfacial polymerization (IP) to obtain regenerated cellulose nanofiltration membranes (IP–ZrO$_2$/BC–NFMs) that exhibited high water flow and rejection of salts and dyes. During interfacial polymerization, anhydrous piperazine (PIP) was used as the waterborne monomer, and 1,3,5-trimesoyl chloride (TMC) and n-hexane were used as the organic phase. The procedure was adjusted by analyzing the impacts of the concentrations of the water and organic phase monomers and the reaction duration on the performance of the developed IP–ZrO$_2$/BC–NFMs. The chemical structures and morphologies of the as-obtained IP–ZrO$_2$/BC–NFMs were examined using various characterization techniques. The performance of these membranes for removal of inorganic salts and dyes as well as their water flow were investigated. IP–ZrO$_2$/BC–NFMs obtained at a pressure of 0.5 MPa, PIP concentration of 1.5 wt.%, TMC concentration of 0.15 wt.%, and polymerization period of 2 min displayed the highest water flux (55.12 LMH) and the best desalination effect (NaCl rejection rate = 19.15%). Over 90% of both Methyl Blue (MB) and Congo Red (CR) dyes were intercepted. We demonstrated that the addition of ZrO$_2$ to nanofiltration membranes significantly enhanced the water flow of the IP–ZrO$_2$/BC–NFMs as well as the salt ion rejection rate.

Keywords: regenerated cellulose; nanofiltration membrane; rejection rate; interfacial polymerization

1. Introduction

Membrane technology, with high efficiency, low-cost, and an environmentally friendly process, has attracted tremendous attention in wastewater treatment. Membrane filtration processes were usually classified as reverse osmosis (RO) technology, nanofiltration (NF) technology, and ultrafiltration (UF) technology according to their membrane pore size [1–5]. Among them, the nanofiltration membranes (NFMs) have been increasingly used in the application of wastewater reclamation, water softening, and desalination due to the excellent water permanence, high retention ability, and energy efficiency.

Interfacial polymerization (IP) is the most popular technique for producing composite NFMs [6]. In IP, phase IP is performed on a suitable substrate, and the reactants polymerize at the immiscible two-phase interface to produce membranes [7]. Typically, two or more active monomers in the aqueous and organic phases are used, and a thin polyamide layer is produced at the phase interface, which increases the salt rejection rate of the membrane, thus preserving and enhancing membrane flow [6]. The NFM layer may be as thin as a few hundred nanometers, which significantly increases the permeability of the membrane and minimizes the pressure difference and operating pressure. Moreover, the irregular pleats enhance the effective area of the filter, substantially enhancing the filtration capacity [8].

Zhou et al. [9] constructed a sercin/TMC active layer on the polysulfone (PSf) membranes via an IP process between sercin and TMC for selective separation of dyes/salts. After the modification of sercin and TMC, the sercin/TMC membrane showed a higher dyes rejection (above 80.8%) and salts rejection (above 20.5%). The influent concentration of salt and dye is set to 100 mg/L and 500 mg/L, respectively. In addition, the obtained
sericin/TMC membrane still remained at a high pure water flux of 65.0 LMH. Mah et al. [10] synthesized a thin–membrane composite (TFC) NFM via IP using triethanolamine (TEOA) and TMC; the TFC–NFM demonstrated superior xylose–to–glucose separation performance compared to commercial membranes. Hao et al. [11] reported an inner bridge strategy for adding Ca\(^{2+}\) during IP using PSf substrates; this strategy stimulated the structural binding of Ca\(^{2+}\)–carboxyl groups on the polyamide separation layer of NFMs and exhibited outstanding antifouling performance.

Cheng et al. [12] employed 4–dimethylaminopyridine (DMAP) as a catalyst for the IP of pentaerythritol (PE) with TMC for enhancing membrane performance. A series of NFMs with varying DMAP contents was created. The outcomes of the filtering tests indicate that the water permeability of the membrane with 40% DMAP was 3.47 times greater than that of the original membrane, and there was no visible salt loss, demonstrating that DMAP can effectively enhance water permeability of IP–PE–DMAP–TMC NFMs. The PE–DMAP–TMC TFC membranes exhibited excellent dye separation and antifouling properties. Ma et al. [13] created a new zwitterionic amine monomer by employing polyethylenimine (PEI) and sulfobetaine methacrylate (SBMA) as reactants in a Michael addition process to produce PEI–g–SBMA. The electroneutral zwitterionic NFM (PEI–G–SBMA/TMC) exhibited a water flux of 132 LMH, which was more than twice that of the PEI/TMC membrane without SBMA. The removal efficiencies of the PEI–g–SBMA/TMC membrane for dye, NaCl, and Na\(_2\)SO\(_4\) were 90.6%, 7.1%, and 50.0%, respectively. Compared to the PEI/TMC membrane, the antifouling performance of bovine serum albumin (BSA), sodium alginate (SA), and humic acid (HA) was greatly enhanced. The electroneutral PEI–g–SBMA /TMC membranes exhibited strong organic repulsion, low salt repulsion, and excellent antifouling performance.

Lai et al. [14] developed five composite membranes with varying percentages of graphene oxide (GO); GO nanosheets were embedded in ultra–thin crosslinked polyamide (PA) layers. With the increase in GO content, the number of hydroxyl and carboxyl groups in the PA layer increased, enhancing the attraction of water molecules to the membrane surface. When 0.02 g/m\(^2\) GO was added to the TFN membrane, the removal rates of Na\(_2\)SO\(_4\) and MgSO\(_4\) reached 95.8% and 97.8%, respectively, and the water flow was 31.4% more than that of the membrane without GO. Zhang et al. [15] fabricated composite NFMs on porous polytetrafluoroethylene (PTFE) substrates by combining epigallocatechin–3–galate (EGCG)–polyetherimide (PEI) co–deposition with TMC crosslinking. By adjusting the EGCG–PEI coating duration, EGCG mass ratio, and TMC concentration, the separation performance of the membrane was maximized. The findings demonstrated that the material possessed a negative surface charge and had a molecular weight cut–off of 380 Da (Stokes radius = 0.46 nm), constituting a dense and defect–free selective layer. Due to the high adhesion and excellent interfacial contact of EGCG–PEI, the membrane also displayed remarkable structural stability and long–term operating stability.

Various functional polyamide membranes are popular in the membrane industry. Thus, interfacial copolymerization has been established as one of the most suitable methods for producing NFMs [16].

In this study, ZrO\(_2\)/BCM [17] manufactured by our research group was employed as the basis membrane for fabricating NFMs; anhydrous piperazine (PIP) was used as the aqueous monomer, and TMC and n–hexane were used as the organic phase for IP. By reacting the PIP monomer with the acyl chloride monomer, a crosslinked polyamide active layer was formed on the ZrO\(_2\)/BC–NFMs, producing a new cellulose NFM, labeled as IP–ZrO\(_2\)/BC–NFM. The influence of the aqueous and organic phase and reaction time on the performance of cellulose NFMs was explored systematically, and the ideal process conditions were determined using orthogonal test analyses. The surface chemical compositions and morphologies of the IP–ZrO\(_2\)/BC–NFMs were characterized and analyzed, in addition to the separation performance of the IP–ZrO\(_2\)/BC–NFM for removal of inorganic salt solutions and dyes.
2. Materials and Methods

2.1. Materials

Cellulose at 650 polymerization degrees was obtained from Sichuan Tianzhu Bamboo Resources Development Co., Ltd. (Chengdu, China). The analytical reagent N–methylmorpholine N–oxide (NMMO) was supplied by Hainachuan Technology Development Co., Ltd. (Tianjin, China). Polyethylene glycol (PEG), BSA, MB, and CR dyes and propyl gallate were obtained from Aladdin Chemical Co., Ltd. (Shanghai, China). Sodium chloride (NaCl), sodium sulfate (Na₂SO₄), magnesium chloride (MgCl₂), calcium chloride (CaCl₂), and zirconium dioxide (ZrO₂) were purchased from Maclean Co., Ltd. (Shanghai, China). Deionized water used in all experiments was produced in the laboratory.

2.2. Preparation of the Membranes

First, the temperature of the vacuum drying oven was adjusted to 60 °C; an appropriate amount of BC was dried in it for 23 h before use. Zirconium dioxide (1 wt.%) was added to an 85 wt.% aqueous solution of NMMO and ultrasonically dispersed for 30 min. This mixture was heated to 90 °C and then 3 wt.% of n–propyl gallate was added as an antioxidant. Thereafter, 3 wt.% of the dried BC was dissolved in the mixture and stirred for 3 h at 110 °C. The resultant mixture was defoamed at 90 °C for 6 h, resulting in a brownish–yellow casting membrane liquid.

On the coater, the casting membrane liquid was poured over nonwoven fabric. The scraper was heated to 85 °C, and its speed was regulated at 20 cm/min. The scraped membranes were placed in air for 10 s, followed by 24 h of soaking in deionized water. The membrane was then removed and air-dried to produce regenerated cellulose membranes with a thickness of 500 µm. The as–obtained regenerated and modified cellulose membrane was labeled as ZrO₂/BCM. An unmodified and regenerated cellulose membrane was prepared using the same process but without ZrO₂, and it was designated as BCM. Table 1 displays the compositions of the various composite NFMs.

Table 1. Compositions of the different NFMs.

<table>
<thead>
<tr>
<th>Number</th>
<th>NMMO (g)</th>
<th>H₂O (g)</th>
<th>BC (g)</th>
<th>ZrO₂ (wt.%)</th>
<th>CPIP (wt.%)</th>
<th>CTMC (wt.%)</th>
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</thead>
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<tr>
<td>BCM</td>
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<td>14</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>ZrO₂/BCM</td>
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<td>14</td>
<td>4</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NFM1</td>
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<td>4</td>
<td>1</td>
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<td>NFM2</td>
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<td>4</td>
<td>1</td>
<td>1</td>
<td>0.15</td>
</tr>
<tr>
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<td>1</td>
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<tr>
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</tr>
<tr>
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<tr>
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</tr>
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<tr>
<td>NFM9</td>
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<td>4</td>
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<td>2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Further, ZrO₂/BCM was used as the substrate for producing NFMs using different concentrations of PIP aqueous phase solution and TMC/n–hexane organic phase solution. First, the cellulose ultrafiltration membrane was placed in a glass dish, and the PIP aqueous phase solution was poured on the membrane until the membrane surface was immersed. After allowing some time for reaction, the membrane was removed, and excess water collected on the surface of the membrane was sucked dry. Thereafter, an additional glass dish was placed over the membrane, and the TMC/n–hexane organic phase solution was poured in. After allowing some time for reaction, the membrane was removed and placed on a sheet of filtration paper to absorb the excess moisture; surface moisture was blown off with a blowing ball. Thus, cellulose NFMs were obtained [18]. The NFM prepared using ZrO₂/BCM was labeled as IP–ZrO₂/BC–NFM. Figure 1 presents a diagram of the preparation process.
with deionized water to remove impurities on membrane surface, and then cut into 1–2 cm sized specimens; these were attached to glass slides and pressed flat for further examination. After the cellulose membranes were stabilized for 10 s, the fixed droplet method was employed to determine the static water contact angle (WCA). To reduce experimental errors, each sample was tested three times, and an average value was obtained by testing at least five positions [19].

2.4. Performance of IP–ZrO$_2$/BC–NFM

2.4.1. Contact Angle of IP–ZrO$_2$/BC–NFM

Cellulose membranes preserved in the wet state were removed, cleaned repeatedly with deionized water to remove impurities on membrane surface, and then cut into 1–2 cm sized specimens; these were attached to glass slides and pressed flat for further examination. After the cellulose membranes were stabilized for 10 s, the fixed droplet method was employed to determine the static water contact angle (WCA). To reduce experimental errors, each sample was tested three times, and an average value was obtained by testing at least five positions [19].

2.4.2. Pure Water Flux of IP–ZrO$_2$/BC–NFM

As shown in Figure 2, the membranes were tested for permeability. The membranes were pretreated at a pressure of 0.1 MPa under the test conditions for 30 min until they reached a stable pressure and water output. Thereafter, the amount of water that passed
through the membrane was measured every 3 min [20]. Equation (1) was used to calculate the water flux:

\[ Q_w = \frac{V}{A \cdot t} \]  

(1)

where \( Q_w \), \( V \), \( A \), and \( t \) represent the water flux (LMH), volume of permeate (L), effective area of the membrane (m²), and time required to collect the permeate (h), respectively.

![Membrane filtration system](image)

**Figure 2.** Membrane filtration system: (1) feed inlet; (2) pump; (3) pressure gauge; (4) membrane cell; (5) permeate end; (6) valve.

### 2.4.3. Retention Rate of IP−ZrO₂/BC−NFM

To evaluate the interception performance of the IP−ZrO₂/BC−NFMs, solutions of sodium chloride, sodium sulfate, magnesium chloride, and calcium chloride were prepared at mass concentrations of 500 mg/L. A conductivity meter was used to measure the interception performance at 0.5 MPa. The concentration of inorganic salt ions before and after membrane filtration was compared to determine the rejection rate, \( J \) (calculated using Equation (2)), of the cellulose membranes [21]:

\[ J = \left(1 - \frac{C_1}{C_2}\right) \times 100\% \]  

(2)

where \( J \), \( C_1 \), and \( C_2 \) represent the rejection rate of the membrane (%), initial concentration (mg/L), and filtrate concentration (mg/L), respectively.

To examine the interception of reactive dyes, solutions with 1 g/L of Methyl Blue (MB) and Congo Red (CR) were prepared. The concentration of incoming and outgoing material was measured at 664 nm and 488 nm using an ultraviolet spectrophotometer. The interception of reactive dyes by IP−ZrO₂/BC−NFM was calculated.

### 2.4.4. Molecular Weight Cut−Off of IP−ZrO₂/BC−NFM

The retained molecular weight (NWCO) refers to the molecular weight corresponding to the neutral molecules when the neutral organic molecule rejection rate reaches 90%. Different molecular weights of polyethylene glycol (PEG), initially at a concentration of 1 g/L, were filtered through a membrane separation system at 0.5 MPa. A total organic carbon analyzer (TOC−VCPH) was used to test the PEG concentration before and after feeding, and membrane pore sizes and distributions were determined [22–24].
The aperture probability density distribution function was expressed using Equations (3) and (4):

\[
\frac{dR(r_p)}{dr_p} = \frac{1}{r_p^2 \sigma_p \sqrt{2\pi}} \exp\left[\frac{(lnr_p - \mu_p)^2}{2(lnr_p)^2}\right]
\]

(3)

\[
r_p = 16.73 \times 10^{-12} \times M_w^{0.557}
\]

(4)

where \(r_p\), \(\mu_p\), \(\sigma_p\), and \(M_w\) represent radius (nm), mean effective radius, geometric standard deviation, and molecule (Da), respectively.

2.4.5. Acid and Alkali Resistance of IP–ZrO\(_2\)/BC–NFMs

Solutions with pH of 2 and 10 were prepared by diluting 1 mole of HCl or 1 mole of NaOH with 1 mole of water. Membranes were submerged in acidic and alkaline solutions separately for 5 days to determine the change in membrane water flux and to analyze the acidic and alkaline resistance of the IP–ZrO\(_2\)/BC–NFMs [25].

3. Results and Discussion

3.1. Optimization of IP–ZrO\(_2\)/BC–NFM by Interfacial Polymerization

In IP, PIP and TMC were polymerized to form a polyacryl active layer [26]. The water and oil monomers were crosslinked, and the different monomer structures, monomer diffusion, and reaction rates resulted in polyamide layers with different structures [27]. The thickness and surface charge of the active layer of polyamide influenced NF membrane permeability. Thus, the concentrations of the water and organic phase monomers and the reaction time were optimized and analyzed to prepare high–performance NFMs [28].

Aqueous monomers influence the structural changes of NFMs’ active layers, as illustrated in Figure 3. The concentration of the water phase during the IP process was the determined basis for the number of PIP monomers involved in the reaction. A polyamide crosslinking network was rapidly formed when the PIP monomer diffused to contact the TMC monomer in the organic phase, rapidly forming a polyamide crosslinking network and generating a polyamide active layer. The initial polyamide crosslinked lattice was relatively loose. PIP alone diffused through the grid and continued to react with the TMC monomer, gradually supplementing the polyamide mesh, making it denser and forming a polyamide layer with a specific thickness [29].

![Figure 3](image-url)

**Figure 3.** Influence of PIP concentration on the water flux (\(Q_w\)) and salt filtration performance (\(R_j\)) of NFMs.
The concentration of PIP was increased from 0.5 to 1.5 wt.%; the continuously thickened polyamide thin layer blocked the transmission of water and inorganic salts. The membrane water flux decreased from 61.3 LMH to 54.1 LMH, and the interception of NaCl showed an increasing trend. The subsequent PIP reaction slowed the diffusion to the organic phase with increase in the grid crosslinking degree.

When PIP concentration was >2.0 wt.%, the water flux of IP–ZrO$_2$/BC–NFM increased from 53.7 LMH to 55.6 LMH, and the interception of NaCl decreased from 41% to 29%. This was because, at the beginning of the IP reaction, a high PIP concentration led to the rapid mixing of the organic phase PIP monomer polymerization with the TMC monomer, which led to a mismatch between the reaction diffusion rates of the two monomers; thus, the “limit effect” occurred, which led to incomplete polyamide/networking, forming a polyamide thin layer distribution with structural defects [30].

Under the condition of constant PIP concentration, the effect of increasing the concentrations of TMC from 0.05 wt.% to 0.25 wt.% during the IP was investigated. As shown in Figure 4, with increase in TMC concentration, the overall trend of membrane water flux first decreased and then increased. At low TMC concentration, the TMC monomer was fully polymerized with PIP from the diffused oil–water monomer, forming a polyamide active layer and promoting the growth of the polyamide layer with an increase in TMC concentration.

![Figure 4. Influence of TMC concentration on the water flux ($Q_w$) and salt filtration performance ($R_j$) of NFMs.](image)

Increase in TMC concentration increased the thickness of the polyamide layer, which decreases the water flux [31]. However, when the concentration of TMC was too high, PIP in the aqueous phase was not sufficient for the IP, and it hydrolyzed and destroyed the integrity of the polyamide crosslinked lattice. At a TMC concentration of 0.15 wt.%, the membrane water flux and desalination performance showed opposite trends.

As shown in Figure 5, with the increase in interface reaction time, membrane water flux exhibited a decreasing trend; the PIP monomer and the TMC organic phase monomer were continuously polymerized, which improved the structure of the polymer network and densified the polyamide active layer, as shown by the decrease in membrane water flux from 64.3 LMH to 52.9 LMH. The densification of the polyamide functional layer hindered the diffusion of the aqueous PIP monomer to the organic phase and slowed the polymerization reaction rate, which in turn prevented further significant changes in the
densification of the polyamide layer. Therefore, a longer reaction time implied slower decrease in membrane water flux. At a reaction time of 2 min, the interception rate of NaCl was 19.15%.

Figure 5. Influence of IP reaction time on the water flux ($Q_w$) and salt filtration performance ($R_{j}$) of NFMs.

The preliminary optimum value was obtained via single factor experiment outcomes, and it was used to further optimize the process parameters of IP. Design-expert software was used to design the orthogonal experiment with PIP concentration, TMC concentration, and polymerization reaction time as the independent variables and two set evaluation indexes of membrane water flux and NaCl interception. The outcomes of the orthogonal experiment are presented in Table 2.

Table 2. Results of orthogonal experiments.

<table>
<thead>
<tr>
<th>Number</th>
<th>$C_{\text{PIP}}/\text{wt.%}$</th>
<th>$C_{\text{TMC}}/\text{wt.%}$</th>
<th>T/min</th>
<th>$Q_w$/LMH</th>
<th>$R_{\text{NaCl}}$/%</th>
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</table>
According to the orthogonal test outcomes shown in Table 2, the orthogonal regression model of IP–ZrO$_2$/BC–NFM water flux and the interception of NaCl were obtained (Tables 3 and 4, respectively). The regression model was highly significant and had a high degree of fitting. The TMC and PIP concentration and polymerization reaction time influenced the water flux and desalination performance in that order. A 3D response surface curve was drawn based on the interaction effects of each factor, as shown in Figure 6. According to the regression model, for PIP concentration of 1.5 wt.%, the concentration of TMC was 0.15 wt.%, polymerization reaction time was 2 min, and the membrane water flux and desalination effect of IP–ZrO$_2$/BC–NFM were the best, indicating that the NFM formed by IP exhibited the best performance under these conditions.

**Table 3.** Variance analysis of IP–ZrO$_2$/BC–NFM quadratic polynomial model for water flux.

<table>
<thead>
<tr>
<th>Source</th>
<th>Squares</th>
<th>df</th>
<th>Square</th>
<th>Value</th>
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</tr>
<tr>
<td>C2</td>
<td>0.77</td>
<td>0.77</td>
<td>16.10</td>
<td>16.10</td>
<td>0.0051</td>
</tr>
<tr>
<td>Residual</td>
<td>0.33</td>
<td>0.048</td>
<td>0.026</td>
<td>0.026</td>
<td>0.9934</td>
</tr>
<tr>
<td>Lack of fit</td>
<td>0.006425</td>
<td>0.002142</td>
<td>0.026</td>
<td>0.026</td>
<td></td>
</tr>
<tr>
<td>R–squared</td>
<td>0.957</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Water flux (Y) = 55.48 + 0.51A + 0.016B + 0.10C + 0.04AB + 0.30AC − 0.07BC + 0.78A$^2$ + 0.48B$^2$ + 0.43C$^2$

**Table 4.** Variance analysis of IP–ZrO$_2$/BC–NFM quadratic polynomial model for sodium chloride interception.

<table>
<thead>
<tr>
<th>Source</th>
<th>Squares</th>
<th>df</th>
<th>Square</th>
<th>Value</th>
<th>Prob &gt; F</th>
</tr>
</thead>
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<tr>
<td>Model</td>
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<td>9</td>
<td>1.44</td>
<td>23.49</td>
<td>0.0002</td>
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<tr>
<td>A–CPIP</td>
<td>2.10</td>
<td>1</td>
<td>2.10</td>
<td>34.25</td>
<td>0.0006</td>
</tr>
<tr>
<td>B–CTMC</td>
<td>0.045</td>
<td>1</td>
<td>0.045</td>
<td>0.73</td>
<td>0.4201</td>
</tr>
<tr>
<td>C–T Time</td>
<td>0.031</td>
<td>1</td>
<td>0.031</td>
<td>0.51</td>
<td>0.4985</td>
</tr>
<tr>
<td>AB</td>
<td>0.25</td>
<td>1</td>
<td>0.25</td>
<td>4.07</td>
<td>0.0833</td>
</tr>
<tr>
<td>AC</td>
<td>0.56</td>
<td>1</td>
<td>0.56</td>
<td>9.17</td>
<td>0.0192</td>
</tr>
<tr>
<td>BC</td>
<td>0.000</td>
<td>1</td>
<td>0.000</td>
<td>0.000</td>
<td>1.0000</td>
</tr>
<tr>
<td>A2</td>
<td>6.76</td>
<td>1</td>
<td>6.76</td>
<td>110.25&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>B2</td>
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<td>1</td>
<td>0.086</td>
<td>1.39</td>
<td>0.2764</td>
</tr>
<tr>
<td>C2</td>
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<td>1</td>
<td>2.48</td>
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<tr>
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<td>7</td>
<td>0.061</td>
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</tr>
<tr>
<td>Lack of fit</td>
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<td>3</td>
<td>0.012</td>
<td>0.13</td>
<td>0.9389</td>
</tr>
<tr>
<td>R–squared</td>
<td>0.968</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reject rate (Y) = 38.36 − 0.51A − 0.075B + 0.063C + 0.25AB + 0.38AC − 1.27A$^2$ − 0.14B$^2$ − 0.77C$^2$
Figure 6. Cont.
Figure 6. Effects of TMC and PIP concentration on water flux (a) and desalination effect (c); Effects of TMC concentration and polymerization reaction time on water flux (b) and desalination effect (d).
3.2. Morphology Analysis of IP–ZrO$_2$/BC–NFM

Figure 7a,b illustrate the surface SEM images of ZrO$_2$/BCM and IP–ZrO$_2$/BC–NFM, which were smooth and flat and relatively rough and dense, respectively. After IP of the PIP and TMC monomers, the NFM surface presented a striped folded structure appearance due to the crosslinking of the active monomers at the water–organic phase interface. This corresponded to the polyamide membrane structure reported in literature [32]; furthermore, the changes in the surface morphology of IP–ZrO$_2$/BC–NFM indicated that a polyamide layer was formed. Figure 8 illustrates that the thickness of the polyamide active layer in IP–ZrO$_2$/BC–NFM was approximately 0.89 µm.

![SEM of membrane surface](image1)

Figure 7. SEM of membrane surface ((a,c) ZrO$_2$/BCM; (b,d) IP–ZrO$_2$/BC–NFM).

![SEM of IP–ZrO$_2$/BC–NFM cross-section](image2)

Figure 8. SEM of IP–ZrO$_2$/BC–NFM cross-section.

Membrane surface roughness influences the permeability of water. Atomic force microscopy (AFM) was used to observe the surface roughness of the NFM. As shown in Figure 9, the root mean square roughness (Rq) of ZrO$_2$/BCM was 16.339 nm. After IP, the roughness increased, and the Rq of IP–ZrO$_2$/BC–NFM increased to 84.411 nm. During
IP, the crosslinking between PIP and TMC on the surface ZrO2/BCM formed a polymer network structure and generated a folded polyamide active layer, which was similar to the surface of IP–ZrO2/BC–NFM (Figure 7d).

Figure 9. Cont.
3.3. FT–IR Analysis of IP–ZrO$_2$/BC–NFM

The infrared spectra of BCM, ZrO$_2$/BCM, and IP–ZrO$_2$/BC–NFM are compared in Figure 10. The FT–IR peak of the $-\text{OH}$ stretching vibration peak of IP–ZrO$_2$/BC–NFM at 3378.03 cm$^{-1}$ was significantly reduced, showing that the polyamide layer formed as viewed from the surface the cellulose ultrafiltration membrane after IP led to fewer hydroxyl groups on the membrane surface and increased the WCA.
During the IP process, the amino of piperazine in the aqueous phase was polymerized with the carboxyl group of homophentriacyl chloride in the organic phase, and the resulting amide group made the elongation vibration of IP–ZrO$_2$/BC–NFM at 1630 cm$^{-1}$ significantly stronger than that of the former two. The stretching vibration of the C–N group in IP–ZrO$_2$/BC–NFM at 1446 cm$^{-1}$ indicated that, on the surface of the cellulose membrane, a thin layer of polyamide was successfully formed. Furthermore, high vibration peaks were observed for C–O and C=O at 1630 cm$^{-1}$ and 1061.02 cm$^{-1}$ in FT–IR spectra, proving that IP did not change the chemical composition of the cellulose membranes [33].

3.4. XRD of IP–ZrO$_2$/BC–NFM

As shown in Figure 11, BC, ZrO$_2$/BCM, and IP–ZrO$_2$/BC–NFM have different XRD patterns. XRD patterns of the NF cellulose membrane were the same as those of the ultrafiltration cellulose membrane, and three crystal planes of cellulose were observed at 2θ = 16.26°, 22.78°, and 26.04°. After IP with ZrO$_2$/BCM as the base membrane, the XRD pattern did not change considerably, no new diffraction peak appeared, and ZrO$_2$/BCM crystallized in a similar manner to IP–ZrO$_2$/BC–NFM.
3.5. TGA Analysis of IP–ZrO$_2$/BC–NFM

According to Figure 12, TGA and DTG images of BC, BCM, ZrO$_2$/BCM, and IP–ZrO$_2$/BC–NFM were used to analyze the thermal stabilities of the materials. The thermal decomposition of cellulose and cellulose membranes occurs in three stages. When the temperature increased to 100 °C, water on the surface evaporated, there was some degradation, and the mass loss of the first three was particularly obvious.

Cellulose, hemicellulose, and organic materials decomposed at 300–500 °C, as observed based on the considerable weight loss in Figure 12 [34,35]. After 500 °C of decomposition until the residual mass, the initial decomposition temperatures of the first three were 204.07 °C, 150.73 °C, and 201.86 °C, respectively, and the initial decomposition temperature of IP–ZrO$_2$/BC–NFM was 251.1 °C, showing that it had higher thermal stability than that of ZrO$_2$/BCM. IP on the surface of ZrO$_2$/BCM resulted in strong interaction between the base membrane surface and the active layer of polyamide, thereby improving thermal stability of the membrane.

3.6. Performance Test of IP–ZrO$_2$/BC–NFM

The static WCA was employed to assess the membrane’s hydrophilicity; a hydrophilic membrane surface helps improve membrane permeability. As depicted in Figure 13, IP–ZrO$_2$/BC–NFM’s WCA was 45.6° ± 2.4°. The molecular structure of cellulose was rich in hydroxyl groups, so it showed high hydrophilicity. After IP, a thin layer of polyamide was developed on the surface of the cellulose membrane, covering the hydroxyl groups and increasing the thickness of the membrane, thus decreasing its hydrophilicity. Compared with the preparation of regenerated cellulose NF membrane by Li [36], the introduction of ZrO$_2$ material into the cellulose membrane increased the rough of the membrane surface structure. Consequently, during IP, improvements were made in the surface morphology of the membrane polyamide layer, resulting in an obvious fold structure, increase in roughness, and improvement in hydrophilicity of the membranes.
Figure 13. Images of the contact angle of BCM, ZrO$_2$/BCM, and IP–ZrO$_2$/BC–NFM.

To evaluate the pore size of the NFM, different molecular weights of PEG were tested for their interception effects. A smaller pore size was more beneficial to the separation performance of the membrane. Figure 14 shows that the intercepted molecular weight of IP–ZrO$_2$/BC–NFM was 692 Da, and the calculated membrane aperture was 0.638 nm.

Figure 14. Molecular weight cut-off of IP–ZrO$_2$/BC–NFM.

NFMs can effectively remove polyvalent salt ions and dye molecules in water, and they are mostly used in water treatment applications such as seawater desalination and softening of drinking water [37]. In this study, 500 mg/L of NaCl, Na$_2$SO$_4$, MgCl$_2$, and CaCl$_2$ and 1000 mg/L of MB (MB 799) and CR (CR 696.663) were used to test the separation performance of IP–ZrO$_2$/BC–NFM at a pressure of 0.5 MPa.

The typical ion selectivity of NFMs resulted from a synergistic interaction between pore size screening in combination with charge repulsion (Donnan effect). The separation performance of IP–ZrO$_2$/BC–NFM is illustrated in Figure 15a. The interception of the inorganic salt solution was in the following order (descending): R(Na$_2$SO$_4$) > R(MgCl$_2$) > R(CaCl$_2$) > R(NaCl). In the NFM, the surface contained negatively charged groups. Under the same test conditions, the inorganic salt solution with high anion content was more repulsive and easily retained. Therefore, for an inorganic salt solution with the same cation, the rejection rate for bivalent salt was much higher than for monovalent salts. The
interception rates of IP–ZrO$_2$/BC–NFM for Na$_2$SO$_4$ and NaCl were 89.12% and 19.15%, respectively, which were in line with the ion selective separation of the NF membrane.

![Graph](image)

**Figure 15.** (a) Interception of inorganic salt solution by ZrO$_2$/BC–NFM; (b) interception of dye by ZrO$_2$/BC–NFM.

MgCl$_2$ and CaCl$_2$ salt solutions have the same anions and the same charged cations. The rejection rate of MgCl$_2$ (27.02%) was higher than that of CaCl$_2$ (21.58%) because the hydration radius [38] of Mg$^{2+}$ was larger than that of Ca$^{2+}$. The separation performance of IP–ZrO$_2$/BC–NFM dye is shown in Figure 15b. Comparing the dye color before and after filtration, an obvious decolorization effect was observed; for MB and CR, the rejection rate was >90%. These filtration experiments on inorganic salt solutions and dyes demonstrate the strong separation performance of IP–ZrO$_2$/BC–NFM [39].

### 3.7. Acid and Alkaline Resistance of IP–ZrO$_2$/BC–NFM

To adapt to different water treatment scenarios, the acidic and alkaline resistance of membrane were explored, which provided insights for expanding the application of membrane in water treatment. At 25 °C and 0.5 MPa, the performance of IP–ZrO$_2$/BC–NFM under acid–base conditions was explored, as shown in Figure 16. After 5 days of static immersion under acidic and alkaline conditions, a decrease in the interception rate for Na$_2$SO$_4$ was observed, despite increases in water flux and WCA for IP–ZrO$_2$/BC–NFM.

![Graph](image)

**Figure 16.** IP–ZrO$_2$/BC–NFM under acidic–alkaline conditions (pH values of 2 and 10): (a) membrane flux and Na$_2$SO$_4$ rejection; (b) contact angle.
Under acidic conditions, the water flux of IP–ZrO$_2$/BC–NFM increased to 67.3 LMH, which could maintain good stability. Under acidic conditions, the nitrogen and oxygen atoms of the amide group are protonated, which affects the electronic field across the nitrogen atom and the carbonyl π–co bond, which weakened the structural stability of the polyamide active layer and destroyed the structure of the polyamide NF membrane composite layer, thereby increasing the membrane water flux and WCA [40,41].

Huang Jiachen [42] also reported that the NFM’s pore size and water flux increased after acid resistance test. Furthermore, the H$^+$ provided by the acidic solution neutralized the negative charge on the surface of IP–ZrO$_2$/BC–NFM, and the charge repulsion effect of the NFM was weakened, thus showing that IP–ZrO$_2$/BC–NFM decreased the interception of inorganic salt ions. Compared to the acidic condition, the change in the performance of IP–ZrO$_2$/BC–NFM was more obvious under alkaline conditions. This was because, in addition to the damage caused by strong alkali on the surface of IP–ZrO$_2$/BC–NFM, the alkaline solution caused swelling of membrane pores, thus significantly reducing the membrane flux. Under alkaline conditions, the membrane pore swelling effect led to a lower rejection rate for the divalent cation [29]. Thus, IP–ZrO$_2$/BC–NFM showed good acidic and alkaline resistance, and it was improved by adding nano ZrO$_2$ particles into the base membrane.

4. Conclusions

This study investigated the preparation of IP–ZrO$_2$/BC–NFMs obtained by IP on ZrO$_2$/BCM, and the effects of water phase monomer concentration, organic phase monomer concentration, and the reaction time on the performance of the NFMs were examined, and the process was optimized. IP–ZrO$_2$/BC–NFMs were synthesized under optimal conditions (concentration of 1.5 wt.% PIP in the water phase, water treatment time of 20 min, concentration of 0.15 wt.% TMC in the organic phase, and reaction time of 3 min). At a pressure of 0.5 MPa, the retention rates for NaCl, Na$_2$SO$_4$, CaCl$_2$, and MgCl$_2$ were 19.15%, 89.12%, 21.58%, and 27.02%, respectively, and the rejection rates of CR and MB were >90%. In addition, under acidic conditions, the water flux of IP–ZrO$_2$/BC–NFM increased to 67.3 LMH, which could maintain good stability.

The above filtration experiments on inorganic salt solutions and dyes showed that the IP–ZrO$_2$/BC–NFMs exhibited strong separation performance as well as good acidic and alkaline resistance.

**Author Contributions:** R.W.: supervision, writing—reviewing and editing, project administration, and funding acquisition. F.T.: methodology, investigation, writing—original draft, data curation, visualization, and supervision. X.H. and G.C.: investigation and data curation. All authors have read and agreed to the published version of the manuscript.

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**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data presented in this study are available on request from the corresponding author.

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