

Article

Experimental and Theoretical Study of Ammonium Nitrogen Adsorption on Natural Zeolite Using Synthetic and Real Reverse Osmosis Pretreated Landfill Leachate

Eleftherios Mamalis ¹, Christina Vasiliki Lazaratou ^{1,2,*} , Varvara Sygouni ¹ , Athanasia G. Tekerlekopoulou ³ 
and Dimitris V. Vayenas ^{1,4,*} 

¹ Department of Chemical Engineering, University of Patras, GR-26504 Patras, Greece; lefmam21@gmail.com (E.M.); sygouni@upatras.gr (V.S.)

² Research and Development Department, Watera Hellas S.A., 13341 Athens, Greece

³ Department of Sustainable Agriculture, University of Patras, 30100 Agrinio, Greece; atekerle@upatras.gr

⁴ Foundation for Research and Technology, Hellas, Institute of Chemical Engineering Sciences, FORTH/ICE-HT, 26504 Patras, Greece

* Correspondence: c.lazaratou@ac.upatras.gr (C.V.L.); dvayenas@upatras.gr (D.V.V.)

Abstract

Natural zeolite was investigated for ammonium nitrogen ($\text{NH}_4^+\text{-N}$) removal from both synthetic aqueous solutions and real pretreated landfill leachate using batch and continuous-flow systems. Batch experiments were conducted at initial $\text{NH}_4^+\text{-N}$ concentrations ranging between 5 and 35 mg/L and zeolite dosages ranging between 10 and 50 g/L. Additionally, real pretreated landfill leachate (35 mg/L $\text{NH}_4^+\text{-N}$) was treated using zeolite dosages of 10–75 g/L, achieving removal efficiencies up to 94%. Equilibrium and kinetic data were analyzed using Langmuir and Freundlich isotherms and pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models. The Freundlich isotherm and PSO model best described the experimental data, indicating heterogeneous, multilayer adsorption governed primarily by chemisorption mechanisms. Continuous fixed-bed column experiments were performed under various flow rates, initial $\text{NH}_4^+\text{-N}$ concentrations, and zeolite masses. The resulting breakthrough curves were modeled using the Clark and modified Clark models, with the modified form showing improved predictive performance. The experimental data were further utilized to develop a MATLAB-based global fitting algorithm incorporating shared parameters across operating conditions. The model demonstrated strong predictive capability for fixed-bed breakthrough behavior. Overall, the results highlight the effectiveness of natural zeolite applicability as a low-cost and efficient post-treatment adsorbent for ammonium removal from complex wastewater streams.

Keywords: ammonium removal; landfill leachate; adsorption; zeolite; modeling



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1. Introduction

Waste disposal in landfills is a widely adopted practice but poses significant environmental risks [1,2]. Landfill leachate contains high organic loads, ammonia, heavy metals and microbial contamination. Organic concentrations are highest in the early aerobic phase and then decrease, stabilizing during the methanogenic phase [2,3]. Approximately 80% of the organic matter is dissolved. Degradation of organic waste also produces methane, contributing to air pollution [4]. Total nitrogen in landfill leachate is dominated by ammonium nitrogen. Unlike soluble organic compounds, the release of soluble nitrogen

from solid waste into leachate occurs over a much longer period [3]. Ammonia nitrogen, commonly reported as $\text{NH}_4^+\text{-N}$, is a characteristic constituent of landfill leachate and is produced primarily through the biological degradation of amino acids and other organic nitrogen-containing materials. The concentration values of other substances, including phosphorus and chloride, vary depending on seasonal conditions [3,5]. In general, landfill leachate contains a high proportion of biodegradable organic matter and exhibits low pH in the early stages, with pH increasing over time as COD declines [6–8].

Variability in the concentrations of leachate constituents complicates leachate management, making necessary the application of diverse treatment processes, such as aerobic [9] or anaerobic [10,11] biological treatment methods, physicochemical treatment processes including adsorption, coagulation–flocculation, membrane filtration, and advanced oxidation processes [12–15], each exhibiting unique strengths and limitations, with no singular universally optimal solution currently established [2,5,7]. Hybrid treatment systems combining adsorption with other processes have shown promising performance [16–18]; however, their optimization and scale-up remain challenging due to the variability of leachate composition and operating conditions.

Among these, adsorption has attracted significant interest, especially for $\text{NH}_4^+\text{-N}$ removal, due to its operational simplicity, high removal efficiency and suitability for polishing or post-treatment applications [16,19,20]. Reviews on landfill leachate management report that membrane processes such as reverse osmosis substantially reduce pollutant concentrations (COD parameter and heavy metal concentrations higher than 98 and 99%, respectively) but may leave residual ammonium, thus requiring a tertiary post-treatment step [21,22]. In this context, adsorption provides a final barrier that stabilizes effluent quality and improves compliance with discharge limits. Natural zeolites are especially suitable because they selectively remove ammonium through ion-exchange mechanisms, whereas carbonaceous adsorbents preferentially target persistent organic compounds [22]. Adsorption using materials such as activated carbon, geopolymers and zeolites (natural or modified) is widely applied for the removal of organic and inorganic pollutants, heavy metals and micro-pollutants from various synthetic and real wastewaters, including landfill leachate [23,24]. Numerous studies have demonstrated the effectiveness of natural zeolites [25], particularly clinoptilolite for $\text{NH}_4^+\text{-N}$ removal from synthetic wastewater and landfill leachate using batch [26,27] or column reactor systems [28,29].

However, the majority of existing studies have focused on batch experiments. In most of these studies, satisfactory performance has been reported, indicating that zeolite is indeed a suitable adsorbent for $\text{NH}_4^+\text{-N}$ removal. Batch studies have been widely preferred by researchers to examine the effects of parameters such as pH, initial $\text{NH}_4^+\text{-N}$ concentration, adsorbent characteristics and contact time [25]. For real untreated landfill leachates, removal efficiencies of up to approximately 66% and 52% have been reported by Genethliou et al. [30] and Vollprecht et al. [31]. Adsorption behavior in such batch systems has commonly been described using equilibrium isotherm models (primarily Langmuir and Freundlich), kinetic models (most often pseudo-first-order (PFO) and pseudo-second-order (PSO)), and thermodynamic analysis, collectively confirming the effectiveness of zeolites as physical adsorbents for ammonium nitrogen removal [27].

Batch tests are commonly used at the laboratory scale, whereas column studies are required for continuous $\text{NH}_4^+\text{-N}$ removal at higher scales. In continuous fixed-bed systems, adsorption performance is strongly influenced by operating conditions such as influent concentration, flow rate, bed height and empty bed contact time (EBCT) [32]. Higher flow rates reduce contact time and accelerate bed saturation, whereas increased bed height provides more active sites and prolongs breakthrough time [33,34]. Influent concentration controls the mass transfer driving force and temperature affects adsorption thermodynam-

ics and diffusion [32]. Previous studies have investigated $\text{NH}_4^+\text{-N}$ removal using zeolite columns treating real landfill leachate [29] or synthetic wastewater [35,36]. Some studies also analyzed breakthrough behavior. Under continuous flow, it is commonly described using the Adams–Bohart, Thomas, Yoon–Nelson and Clark models, which represent mass transfer and adsorption dynamics with different complexity levels [36–38].

In these adsorption column studies, breakthrough models are fitted independently for each operating condition, resulting in condition-specific parameters that cannot be transferred to new systems without additional experiments. A recent study by Singh et al. [39] developed a predictive mathematical model for fixed-bed adsorption columns that relates reactor operating parameters (bed height, flow rate, and influent concentration) to the breakthrough curve. However, the model was built primarily from column breakthrough data and relied on empirical correlations between parameters and operating variables that were then confronted with experimental data (obtained from published research papers, e.g., ammonia ion adsorption on Jordanian zeolite, Pb(II) on *Auricularia* matrix waste and acid yellow 17 dye on tamarind seed powder) and adjusted using tools of machine learning. Myers et al. [40] also examined pollutant adsorption in a fixed-bed/packed adsorption column using coupled heat and mass transfer modeling, however, for the adsorption of toluene on activated carbon (dominated by physical adsorption) and Cr(III) on zeolite NaX (dominated by ion exchange). The authors showed that predicting breakthrough curves accurately requires simultaneous fitting of transport parameters and adsorption equilibrium/kinetic constants, because temperature and concentration fronts move together inside the bed. The model was validated against experimental breakthrough data and demonstrated that using independent (separate) fitting leads to large parameter errors, while global fitting to the whole curve reproduces the adsorption front and saturation time well.

In this study, $\text{NH}_4^+\text{-N}$ adsorption onto natural zeolite was investigated using synthetic ammonium solutions and real reverse osmosis (RO) pretreated landfill leachate in batch and continuous fixed-bed column systems. Rather than treating the experimental work as an isolated adsorption assessment, the experiments were designed to generate a dataset for model development and validation. Experimental data from batch and column studies were used to parameterize adsorption isotherms and kinetics, while continuous-flow data were interpreted using an established and modified breakthrough model. A global fitting algorithm with shared parameters, implemented in MATLAB R2025a (provided by University of Patras), was developed to link model constants to initial operating conditions, enabling reliable prediction of column performance beyond the experimental range. This integrated experimental–modeling framework enhances the practical applicability of zeolite-based adsorption and provides a robust tool for the design and optimization of landfill leachate treatment systems. Accordingly, the aim of this study is to evaluate the role of natural zeolite adsorption as a polishing step for reverse-osmosis-treated landfill leachate and to develop a predictive modeling tool capable of estimating ammonium removal and breakthrough behavior under variable operating conditions. By coupling experimental data with a global fitting algorithm, the study seeks to provide a practical method for predicting effluent concentrations and verifying compliance with regulatory discharge limits prior to full-scale implementation.

2. Materials and Methods

2.1. Synthetic Aqueous Solutions and Real Landfill Leachate

Synthetic solutions (SSs) were prepared by drying ammonium chloride at 105 °C for 24 h and then dissolving it with deionized water (DW) to concentrations ranging from 5 to 50 mg/L. Real landfill leachate (LL) was supplied by a municipal sanitary landfill and

collected from the outlet of a reverse osmosis (RO) membrane module. $\text{NH}_4^+\text{-N}$ was the main cation in the pretreated LL, with concentrations ranging between 5 and 50 mg/L and a pH of 7.7. LL samples were kept at 4 °C for the duration of the experimentation period.

2.2. Adsorbent

Natural zeolite was provided by S&B Industrial Minerals AD (Athens, Greece), situated in the Rhodope Prefecture (Greece), which provided the chemical composition of the sample (Table 1). Sieved natural zeolite with particle sizes smaller than 50 µm was washed with distilled water and dried at 60 °C. The mineralogical composition of powdered zeolite was identified with powder X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer Bruker Corporation, Karlsruhe, Germany) operating with Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda = 0.154059$ nm). XRD patterns were obtained over a 2θ range of 2° to 70° at a scanning rate of 2°/min. The N_2 physisorption was performed in a Quantachrome iQ series apparatus (Anton Paar QuantaTec Inc., Boynton Beach, FL, USA) using 0.097 g of the zeolite sample, which was degassed at 90 °C under vacuum for 3 h and then re-weighed before the measurements of N_2 adsorption at 77 K. The Brunauer–Emmet–Teller (BET) equation was applied in the range of 0.05–0.3 P/P0 to calculate the specific surface area (SSA). The total pore volume and pore distribution were determined as well using the DFT method. The FTIR (Fourier Transform Infrared Spectroscopy, Shimadzu IR Tracer–100 spectrometer, Shimadzu, Kyoto, Japan) method was used to determine the chemical groups present on the surface of the raw material and after saturation from breakthrough experiments.

Table 1. Chemical composition of the raw zeolite sample.

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Loss of Igniton (1050 °C)
%	69.52	13.52	0.71	3.25	0.88	0.54	2.90	8.21

2.3. Batch Adsorption Experiments

A series of batch adsorption experiments using natural zeolite were conducted to evaluate the removal of $\text{NH}_4^+\text{-N}$ from both the SSs and LL. For each batch experiment, 200 mL of SSs or LL was placed in a 600 mL beaker, and zeolite was added at various adsorbent-to-solution mass ratios. The tests were performed using a jar tester (VELP Scientifica, Usmate Velate, Italy) at a stirring speed of 200 rpm at room temperature (25 ± 1 °C) (Figure S1a). Initially, adsorption experiments were performed using SSs with initial $\text{NH}_4^+\text{-N}$ concentrations of 5, 15 and 35 mg/L. NH_4Cl was dissolved in deionized water to prepare a 100 mg/L ammonium stock solution, which was subsequently diluted to the desired concentrations for the batch studies. Zeolite dosages of 1, 5, 10, 20, 40 and 50 g/L were evaluated in 1 h adsorption experiments to determine the optimum zeolite dosage. After equilibrium was reached, the concentration of $\text{NH}_4^+\text{-N}$ in the supernatant was measured.

Subsequently, the LL with an initial $\text{NH}_4^+\text{-N}$ concentration of 35 mg/L was examined at zeolite-to-solution ratios of 10, 20, 40, 50 and 75 g/L. The effect of pH was also investigated within the range of 6.5–8.5. The solution pH was adjusted using standard sulfuric acid (H_2SO_4) or sodium hydroxide (NaOH) solutions. The zeolite dosage in these experiments was 50 g/L. The adsorption capacity, q_e (mg/g) and removal efficiency were calculated using the following equations:

$$q_e = \frac{(C_0 - C_e) \cdot V}{W} \quad (1)$$

$$\text{Removal efficiency}(\%) = \frac{(C_0 - C_e)}{C_0} \cdot 100\% \quad (2)$$

where V is the volume of the SS or LL (L), W is the mass of the adsorbent (g), and C_0 and C_e are the initial and equilibrium NH_4^+ -N concentration (mg/L) in the SS or LL.

2.4. Continuous-Flow Adsorption Experiments

Continuous adsorption of NH_4^+ -N onto zeolite was investigated using fixed-bed column experiments. Plexiglas columns with a height of 40.0 cm and an internal diameter of 4.0 cm, equipped with four sampling ports at different heights along the column, were employed (Figure S1b). The column dimensions remained constant; however, different zeolite masses (80, 120, and 160 g) were packed into the column, resulting in different packed-bed heights and corresponding bed volumes. The zeolite was sieved to obtain a particle size of 1.0–1.8 mm, rinsed with distilled water to remove impurities and dried at 105 °C prior to use. The SS was introduced through the zeolite bed in an upward-flow mode using a peristaltic pump (company). Experiments were carried out at different adsorbent-to-solution ratios (10, 20, 40, 50, and 75 g/L) and at various pH values. Samples were collected at predetermined time intervals and analyzed to determine residual NH_4^+ -N concentrations. The effects of key operating parameters were evaluated, including initial NH_4^+ -N concentrations (15, 35, and 50 mg/L), the bed volume corresponding to different zeolite masses (80, 120, and 160 g), and flow rates (10 and 20 mL/min).

2.5. Analytical Methods

SS or LL samples were collected at different time intervals, centrifuged at 5500 rpm for 2 min to remove suspended solids and subsequently filtered through 0.45 µm membrane filters (Whatman, Cytiva, Amersham Place, Little Chalfont; Cardiff, UK). NH_4^+ -N was measured according to the modified Salicylate method of Verdouw et al. [41] described in detail by Genethliou et al. [42]. After color development, the optical absorption of the solution was measured at 625 nm with a UV–VIS spectrophotometer (Hach Lange, DR-500, Hack, Loveland, CO, USA). All chemical reagents were of high analytical grade and were used without further purification. All experiments were conducted in duplicate.

2.6. Theoretical Modeling of Batch and Column System

2.6.1. Batch Systems

Adsorption Isotherm models:

The isotherms of NH_4^+ -N adsorption on zeolite were obtained from the fitting of batch adsorption experimental data using Langmuir and Freundlich models, described by the following equations:

Langmuir

$$q_e = \frac{q_{\max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (3)$$

with the linear form as

$$\frac{C_e}{q_e} = \frac{1}{K_L \cdot q_{\max}} + \frac{C_e}{q_{\max}} \quad (4)$$

Freundlich

$$q_e = K_f C_e^{1/n} \quad (5)$$

with the linear form as

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (6)$$

where q_e is the adsorption capacity (mg/g) of the adsorbent at equilibrium, $q_{\max}$ is the maximum adsorption capacity (mg/g) of zeolite corresponding to the complete monolayer coverage, C_e is the NH_4^+ -N concentration (mg/L) at equilibrium, K_L is the Langmuir

adsorption constant (L/mg) related to the affinity between the adsorbate and binding sites of the adsorbent, n is a number characteristic of the energy distribution function and $K_f((\text{mg/g}) (\text{L/mg})^{1/n})$ is the Freundlich isotherm constant related to the adsorption capacity of zeolite.

Kinetic Models

Kinetic adsorption models can be used to describe the adsorption rate under specific conditions and to determine whether the process is controlled by chemical interactions or diffusion phenomena within the pores. In the pseudo-first-order model (PFO) the adsorbate is assumed to be adsorbed onto a single surface site at a time [43].

The PFO model is given by the equation

$$q_t = q_e (1 - e^{-k_1 t}) \quad (7)$$

while its linear form is defined as

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (8)$$

where q_t (mg/g) is the mass of the adsorbed compound per unit mass of adsorbent, q_e (mg/g) is the final mass adsorbed when the system is at equilibrium, t is the time, and the adsorption rate depends on the constant k_1 (1/min)

The pseudo-second-order model assumes that the adsorbate is adsorbed on two surface sites at time t and that the rate-limiting step (slowest step) is surface adsorption, which involves chemisorption of the adsorbate on the adsorbent. The nonlinear form of the PSO equation is given by the equation

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (9)$$

and its linear form is given by

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

where q_t (mg/g) is the amount of adsorbed compound per unit mass of adsorbent at time t and q_e (mg/g) is the maximum amount adsorbed at equilibrium. The constant k_2 (g/(mg min)) is the regulatory parameter of the model characterizing the rate of chemical adsorption [44].

The correlation coefficient (R^2) was used as a statistical measure to quantify the deviation to measure the uncertainty in the distribution of errors and then determine the most appropriate kinetic/isothermal model. R^2 is given by

$$R^2 = 1 - \frac{\sum_{i=1}^p (q_{e,meas,i} - q_{e,theor,i})^2}{\sum_{i=1}^p (q_{e,meas,i} - q_{e,mean,meas})^2} \quad (11)$$

where i is the experimental run, $q_{e,theor}$ and $q_{e,meas}$ (mg/g) are the theoretically evaluated equilibrium values from the model (mg/g) and the experimentally measured equilibrium data (mg/g), respectively, while $q_{e,mean,meas}$ is the mean of q_e .

2.6.2. Fixed-Bed Reactor System

Kinetic Models

The adsorption experiments that were carried out in the packed-bed column were modeled using several kinetic models: the Thomas kinetic model, Bohart–Adams, Clark, and their modified versions. For all models, the parameters were optimized by minimizing

the residual error between the experimental and model-predicted values with the Microsoft Excel Solver add-in.

The Thomas kinetic model assumes plug flow and is described by the equation

$$\frac{C_t}{C_{in}} = \frac{1}{1 + \exp(k_{Th} q_e \frac{x}{v} - k_{Th} C_{in} t)} \quad (12)$$

where C_t is the concentration of $\text{NH}_4^+\text{-N}$ (mg/L) at the outflow of the packed column at time t (min), C_{in} is the concentration of $\text{NH}_4^+\text{-N}$ at the feed liquid, k_{Th} corresponds to the Thomas rate parameter in mL/(min mg)), x (g) is the mass of the adsorbent in the column and v mL/min is the flow rate.

The Bohart–Adams model is described by the following equation:

$$\frac{C}{C_0} = \exp\left(K_{AB} C_0 t - K_{AB} N_0 \frac{z}{U_0}\right) \quad (13)$$

where C (mg/L) is the concentration of $\text{NH}_4^+\text{-N}$ at the column outlet at time t and C_0 (mg/L) is the $\text{NH}_4^+\text{-N}$ initial concentration at the inlet. K_{AB} (L/(mg min)) is the kinetic constant of the Bohart–Adams model expressing the reaction rate between the pollutant and the adsorbent. N_0 (mg/L bed) is the maximum mass of pollutant that can be retained by the unit volume of the adsorbent material, z (cm) is the height of the adsorption bed and U_0 (cm/min) is the surface flow velocity.

The Clark model combines the kinetic mass transfer theory with Freundlich isotherms, and it assumes that the adsorption process follows a filtration mechanism with a cumulative effect of concentration and that the Freundlich equation describes isothermal equilibrium. The Clark model is described by the equation

$$\frac{C}{C_0} = \frac{1}{[1 + A \exp(-rt)]^{\frac{1}{n-1}}} \quad (14)$$

where C (mg/L) is the $\text{NH}_4^+\text{-N}$ concentration at the outlet, C_0 (mg/L) is the initial concentration, A is a constant related to the breakthrough concentration, breakthrough time, and initial concentration, and determines the slope of the curve, r (1/min) is the kinetic constant of the model, depending on the mass transfer coefficient and the flow velocity, n is calculated by the Freundlich isotherm and expresses the degree of heterogeneity of the adsorption surface (it is lower than 1), and t (min) is the time [45].

The modified Thomas kinetic model assumes that adsorption follows PSO kinetics. The modified version includes parameters taking into account non-ideal flow conditions and anomalies in the distribution of active sites [46].

$$\frac{C}{C_0} = \frac{1}{1 + \exp\left(\frac{kt^{-h} q_0^m}{v} - \frac{kC_0}{1-h} t^{1-h}\right)} \quad (15)$$

where the parameters are the same as in Equation (12) and h is the heterogeneity index ($0 \leq h \leq 1$). In homogenous systems $h = 0$, when $h > 0.5$ strong heterogeneity exists, with diffusion limitations resulting in a very asymmetric curve, probably not reaching full saturation [47].

The modified Bohart–Adams model is used to describe the relationship between the concentration at the outlet and time in a fixed-bed column, considering not only the surface

adsorption but also losses due to diffusion phenomena and bed heterogeneities. This modified equation is

$$\frac{C}{C_0} = \frac{\exp\left(\frac{K_{BA}C_0}{1-h} t^{1-h}\right)}{\exp\left(\frac{K_{AB}t^{-h}N_0z}{u_0}\right) + \exp\left(\frac{K_{BA}C_0}{1-h} t^{1-h}\right) - 1} \quad (16)$$

where the parameters are similar to those in Equation (13) and h is the heterogeneity-parameter-related fractal of the system. Equation (10) applies to diffusion in homogeneous systems for $h = 0$.

The modified Clark model is widely used in cases where traditional theories fail to describe the data adequately.

$$\frac{C}{C_0} = \frac{1}{[1 + A \exp(-\frac{r}{1-h} t^{1-h})]^{\frac{1}{n-1}}} \quad (17)$$

where the parameters are the same as those in Equation (14) and h is the heterogeneity parameter.

2.7. Global Fitting Algorithm with Shared Parameters for the Prediction of NH_4^+ -N Adsorption on Zeolite

The experimental data obtained in this study were used to develop a global fitting algorithm with shared parameters, based on the modified Clark's model, capable of describing and predicting NH_4^+ -N breakthrough behavior. This approach enables improved understanding of the influence of operating parameters on the model constants, which is essential for process optimization and potential industrial application.

The experimental results were compiled into a dataset containing the estimated values of the modified Clark model constants (A , r , and h). The data were divided into two subsets: a training set and a validation set. The training set consisted of five of the eight experimental datasets and was used to develop and calibrate the equations relating the model constants to the operating parameters. The validation set comprised the remaining three datasets and represents intermediate operating conditions.

The inclusion of intermediate values in the validation set was important for evaluating the predictive performance of the model under various conditions. Mathematical relationships describing constants A and r as functions of initial concentration (C_0), flow rate (Q), and zeolite mass were examined. To this end, second-degree polynomial, exponential-linear form, log-linear and log-log formulations were tested. Three evaluation criteria were applied:

- The correlation coefficient (R^2) to assess the goodness of fit to the training data, with values closer to unity indicating better agreement.
- The root mean square error (RMSE) to quantify deviations between predicted and experimental values.
- Deviation from the validation set, assessing the model's ability to predict constant values for experiments not used during training.

2.8. Statistical Analysis

All experimental sets were performed in duplicate, and the results were presented as the mean $\pm$ standard deviation (SD). Each mean value was calculated from two samples taken from two independent experiments characterized by the same operating conditions. Statistically significant differences between data were evaluated using Student's t -test (Microsoft Office Excel 2007, Redmond, WA, USA) confidence interval for 95% probability; thus, a value of $p \leq 5\%$ was considered statistically significant.

3. Results and Discussion

3.1. Adsorbent Characterization

3.1.1. XRD

The XRD pattern (Figure 1) of the investigated sample revealed the presence of a zeolitic phase belonging to the HEU-zeolite structural group, characterized by diffraction peaks at approximately $2\theta \sim 9.8^\circ$, 11.1° , 22.3° , 26° and 29.9° , which are typical of clinoptilolite-rich zeolites [48]. Given the structural similarity between clinoptilolite and heulandite, which form a continuous solid-solution series, and considering the geological origin of the sample (Rhodope zone), the material is identified as a clinoptilolite-rich HEU-type zeolite. This interpretation is consistent with previous studies reporting that natural zeolitic deposits in the Thrace region commonly consist of clinoptilolite–heulandite mixtures, while weaker and overlapping peaks in the $27\text{--}32^\circ$ region may indicate traces of mineral impurities such as feldspars or micas [49].

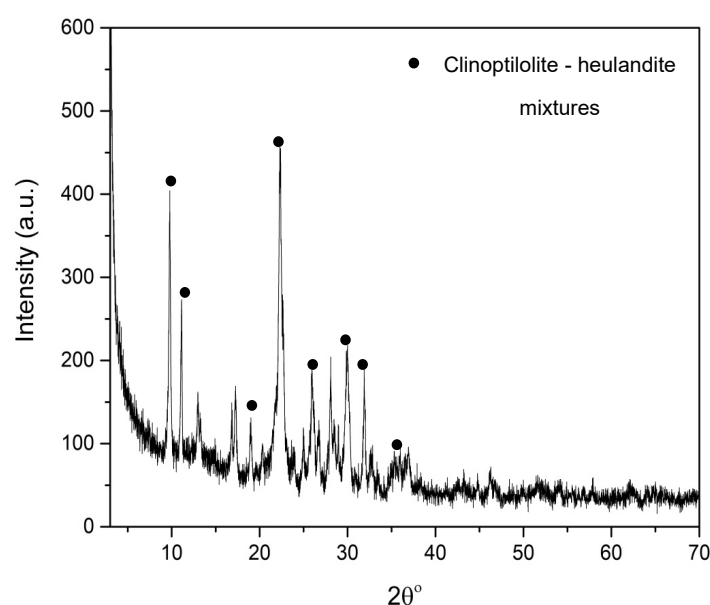


Figure 1. XRD pattern of zeolite sample.

3.1.2. N₂ Physisorption Isotherms

The textural properties of the investigated material were evaluated through N₂ adsorption–desorption isotherms at 77 K (Figure 2a), complemented by BET and DFT analyses. The adsorption–desorption isotherm exhibited a characteristic *Type IV* profile with a pronounced *H3* hysteresis loop, indicative of a predominantly mesoporous structure associated with slit-shaped pores and intraparticle voids. The adsorption branch showed limited uptake at very low relative pressures ($P/P_0 < 0.01$), suggesting a weak contribution of microporosity, while the gradual increase in the intermediate pressure range ($0.05 < P/P_0 < 0.3$) corresponds to multilayer adsorption on the external surface. A steep increase in adsorbed volume at higher relative pressures ($P/P_0 > 0.7$) was observed, which is attributed to capillary condensation within mesopores and larger textural voids. The specific surface area, calculated using the BET equation, was found to be $41.6 \text{ m}^2/\text{g}$, which is significantly lower compared to synthetic zeolites due to structural heterogeneity, extra-framework cations, and limited pore accessibility [50]. Recent studies confirm that natural clinoptilolite-rich minerals commonly display reduced N₂-accessible surface areas despite maintaining a microporous framework, as adsorption is strongly influenced by the presence of exchangeable cations (e.g., Ca^{2+} , Na^+ , Mg^{2+}) and associated hydration layers that partially block pore entrances [51,52]. As a result, the measured surface area primarily

reflects external surface and mesoporous contributions rather than the intrinsic zeolitic microporosity. Similar observations have been reported in recent experimental studies on natural clinoptilolite used for adsorption applications, where N_2 adsorption revealed relatively low surface areas while maintaining high removal efficiencies for pollutants due to ion exchange and surface reactivity mechanisms [52].

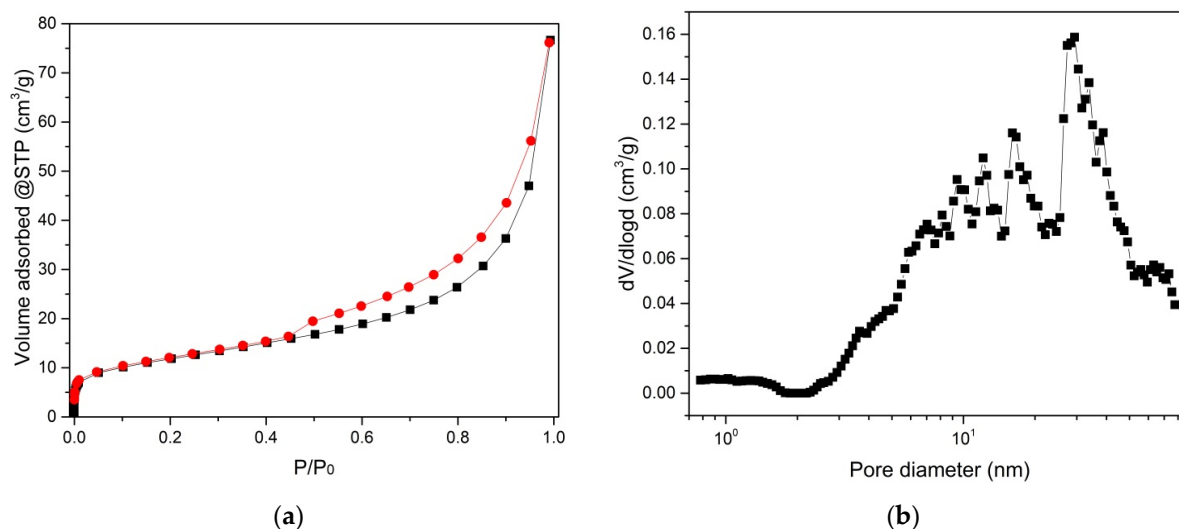


Figure 2. (a) N_2 adsorption (black) and desorption (red) isotherms and (b) DFT pore size distribution on zeolite sample.

The DFT pore size distribution (Figure 2b) revealed a hierarchical structure dominated by mesopores in the range of 2–50 nm, with a primary maximum centered around 5–10 nm and a secondary contribution extending toward larger pore widths (>50 nm), consistent with intraparticle porosity. In contrast, the micropore fraction (<2 nm) was minimal, contributing less than 5% to the total pore volume, in agreement with the limited adsorption observed at very low relative pressures. The total pore volume was estimated at $\sim 0.108 \text{ cm}^3/\text{g}$, confirming that the accessible porosity is largely governed by mesoporous and external surface contributions.

Therefore, the predominance of mesoporous features observed in the present study, together with the limited low-pressure uptake and the broad DFT distributions, indicates that the measured BET surface area primarily reflects external surface and textural porosity, rather than the total intrinsic microporous network. This behavior is characteristic of natural clinoptilolite systems and should be interpreted as a manifestation of restricted pore accessibility rather than poor material quality, in agreement with contemporary literature on natural zeolite adsorption behavior.

3.1.3. FTIR

FTIR analysis provided additional evidence regarding the NH_4^+ adsorption mechanism on the HEU-type zeolite (Figure 3). After adsorption, the emergence of the characteristic band at approximately 1400 cm^{-1} , assigned to the N–H bending vibration of NH_4^+ , confirmed the successful incorporation of ammonium ions onto the zeolite [53,54]. In addition, slight variations in the intensity of the Si–O–Si/Si–O–Al asymmetric stretching band at around 1028 cm^{-1} suggested the participation of the aluminosilicate framework in the adsorption process, while the absence of significant peak shifts or new framework-related bands indicated that the crystalline structure of the zeolite remained essentially unchanged. The relatively high Al content of the HEU zeolite (13.52 wt.% Al_2O_3) generates negatively charged AlO_4^- tetrahedra that are compensated by exchangeable cations, mainly Ca^{2+} ,

K^+ , and Na^+ , as confirmed by the XRF analysis. These cations can be readily exchanged with NH_4^+ ions from solution, indicating that cation exchange constitutes the primary removal mechanism. The preservation of the zeolite framework after adsorption further suggests that NH_4^+ uptake occurred through occupation of existing exchange sites rather than structural alteration of the mineral [55]. This interpretation is consistent with the excellent fit of both the Langmuir and Freundlich isotherm models, indicating adsorption on abundant exchange sites with a certain degree of surface heterogeneity.

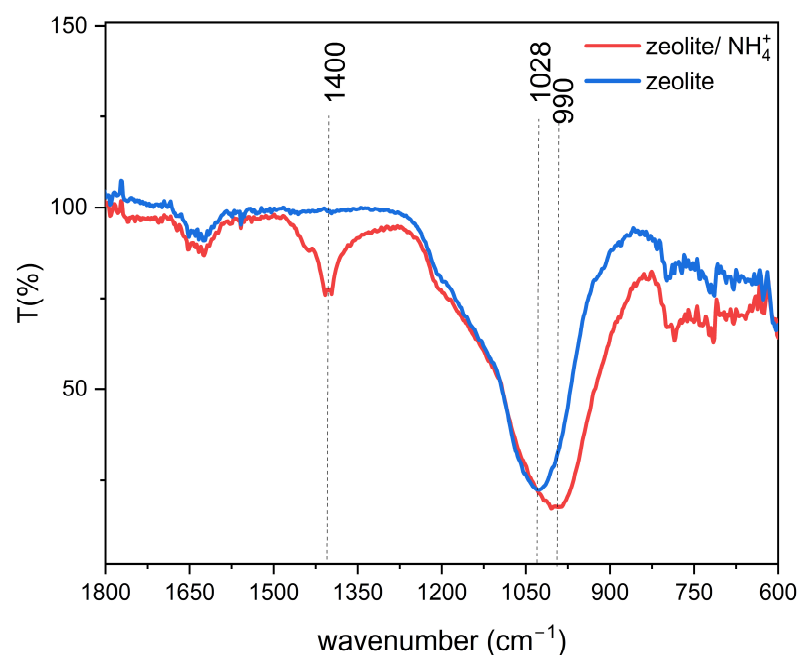


Figure 3. FTIR spectra of raw zeolite sample and NH_4^+ saturated zeolite after breakthrough experiments (focus on the range where N-H bonds were expected).

3.2. Batch Experiments

3.2.1. Effect of Adsorbent Dosage and of Initial NH_4^+ -N Concentration

A series of batch experiments were conducted to estimate the adsorption capacity of zeolite. Initially, the removal of NH_4^+ -N was evaluated using a standard solution with an initial concentration (C_0) of 5 mg/L at zeolite mass-to-solution volume ratios of 1.0, 5.0, 10.0, 20.0, 40.0 and 50.0 g/L. NH_4^+ -N removal increased with increasing zeolite dosage (Figure 4a), and at ratios of 10.0 mg/L and higher the removal exceeded 85% within the first 5 min. Statistical analysis showed that NH_4^+ -N removal differed significantly among the tested zeolite dosages ($p < 0.05$ for all pairwise comparisons up to 60 min) except between 40 and 50 g/L ($p = 0.4634$).

Next, the initial NH_4^+ -N concentration was increased to 15 mg/L and 35 mg/L (Figures 4b and 4c, respectively), and experiments were conducted at zeolite mass-to-solution volume ratios of 10.0, 20.0, 40.0 and 50.0 g/L. In most cases, adsorption occurred rapidly within less than 5 min. Increasing the zeolite mass resulted in higher NH_4^+ -N removal due to the greater number of available adsorption sites. Statistical analysis showed that NH_4^+ -N removal differed significantly among the tested zeolite dosages ($p < 0.05$ for all pairwise comparisons up to 60 min) except between 40 and 50 g/L ($p = 0.2568$ and 0.1107, for initial NH_4^+ -N concentration of 15 mg/L and 35 mg/L, respectively).

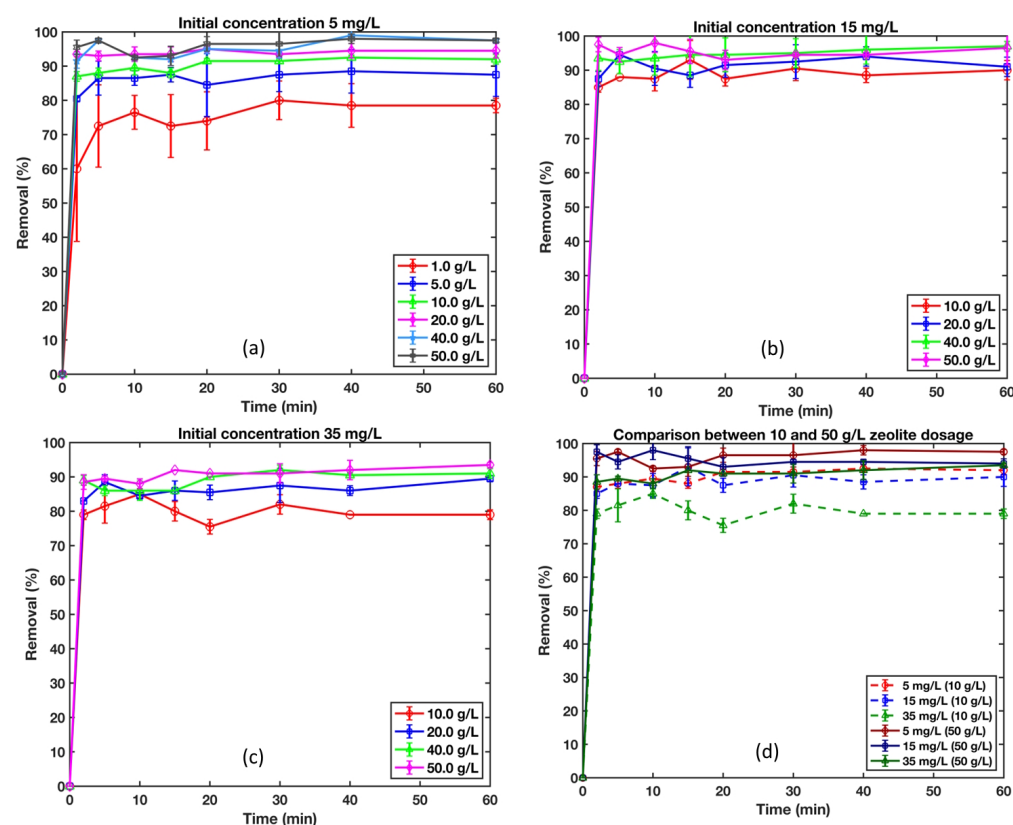


Figure 4. Effect of zeolite mass-to-solution volume ratio on $\text{NH}_4^+\text{-N}$ removal from standard solutions: (a) $C_0 = 5$ mg/L, (b) $C_0 = 15$ mg/L and (c) $C_0 = 35$ mg/L. (d) Percentage ammonium removal from standard solutions at $C_0 = 5, 15$ and 35 mg/L for zeolite mass-to-solution volume ratios of 10.0 and 50.0 g/L.

Regarding the effect of the initial $\text{NH}_4^+\text{-N}$ concentration, no significant differences were observed between initial concentrations of 5 and 15 mg/L at zeolite mass-to-solution volume ratios of 10 and 50 g/L (Figure 4d) ($p = 0.29048$ and 0.6991 for zeolite dosages of 10 and 50 g/L, respectively). Specifically, at 10 g/L, high removal efficiencies were achieved after 30 min, reaching 91.5% and 90.5% for initial $\text{NH}_4^+\text{-N}$ concentrations of 5 and 15 mg/L, respectively, whereas at 50 g/L the removals were 96.5% and 94.5%, respectively. At a higher initial $\text{NH}_4^+\text{-N}$ concentration (35 mg/L), competition for active sites slightly reduced removal at 10 g/L (82%), but this effect was decreased at 50 g/L (91%). Moreover, increasing the zeolite dosage from 10 to 50 g/L significantly improved $\text{NH}_4^+\text{-N}$ removal at all initial concentrations due to the greater number of available ion-exchange sites. Similar trends have been reported in recent studies, where increased zeolite dosage enhanced NH_4^+ removal efficiency due to increased surface area and exchange capacity [49,50].

3.2.2. Effect of pH

According to the literature, the process of ammonium ion exchange from zeolite is influenced by pH, affecting both the change in the chemical form of ammonium (between NH_4^+ and NH_3) and the surface charge of the zeolite [56,57]. At acidic and neutral pH values, ammonia nitrogen exists predominantly as NH_4^+ , which readily participates in cation exchange with the negatively charged sites of the zeolite. As pH increases, the equilibrium gradually shifts toward the uncharged NH_3 species, which cannot be removed by ion exchange [57]. At low pH, H^+ ions also compete with NH_4^+ for the available exchange sites, reducing ammonium removal efficiency. Conversely, moderately alkaline conditions increase the negative surface charge of the zeolite, enhancing electrostatic

attraction toward NH_4^+ , although further increases in pH promote NH_3 formation and may eventually reduce ion-exchange efficiency [56–58].

This study tested the effect of pH on the removal of NH_4^+ -N from real waste (pre-treated landfill leachate). The initial pH of the sample was 7.5, and the effect of pH was evaluated by adjusting it to 6.5 and 8.5. This range was chosen to realistically reflect environmental conditions without introducing extreme pH values that would significantly alter the chemical behavior of ammonium and the stability of zeolite.

As shown in Figure S2, the lowest removal efficiency was observed at pH 6.5 (86%), whereas higher removal efficiencies were obtained at pH 7.5 (91%) and 8.5 (92%). The limited effect of pH within the investigated range is consistent with the predominance of NH_4^+ under these conditions, indicating that only minor changes in ammonia speciation occurred [57]. Therefore, the amount of exchangeable NH_4^+ remained essentially unchanged, and no statistically significant differences in NH_4^+ -N removal were observed among the tested pH values ($p > 0.05$ for all pairwise comparisons up to 20 min). The slightly lower removal at pH 6.5 is attributed primarily to increased competition between H^+ and NH_4^+ for the zeolite exchange sites. Because pH adjustment did not significantly improve ammonium removal, the natural leachate pH (7.5) was selected for all subsequent experiments, thereby avoiding unnecessary chemical addition and minimizing operating costs.

3.3. Adsorption Performance in Real Wastewater Sample

In the next step, landfill leachate after RO treatment was tested at an initial NH_4^+ -N concentration of 35 mg/L, which falls within the typical range of concentrations observed after RO treatment of the unit. Zeolite mass-to-solution volume ratios ranging from 10 g/L to 75.0 g/L were applied (Figure 5a). The percentage removal of NH_4^+ -N increased with an increasing zeolite mass-to-solution volume ratio, reaching up to 92% and 94% at ratios of 50 and 75 g/L, respectively (Figure 5b). Statistical analysis showed that NH_4^+ -N removal differed significantly among the tested zeolite dosages ($p < 0.05$ for all pairwise comparisons up to 60 min) except between 10 and 20 g/L ($p = 0.1906$), as well as between 50 and 75 ($p = 0.3736$).

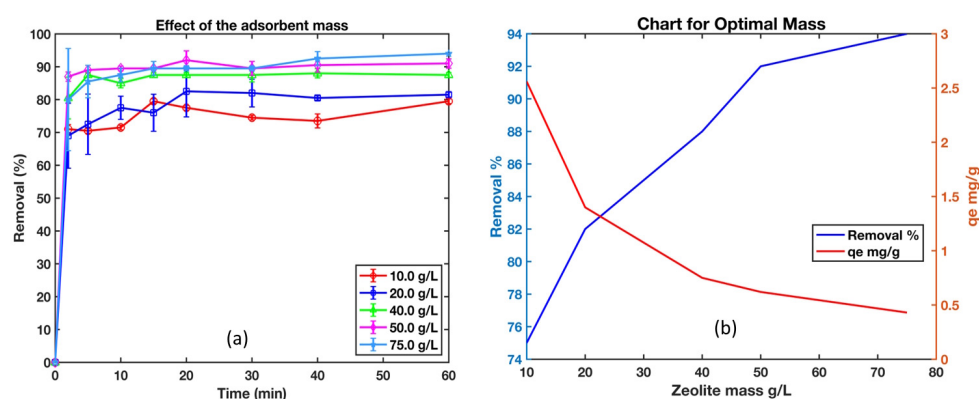


Figure 5. (a) Effect of zeolite mass-to-solution volume ratio on ammonium removal from landfill leachate ($C_0 = 35 \text{ mg NH}_4\text{-N/L}$). (b) Correlation of ammonium removal with zeolite mass-to-solution volume ratio and ammonium ion concentration at equilibrium.

The increase in removal efficiency from 75% to 92% as the adsorbent dosage increased from 10 g/L at 75 g/L reflects the larger total number of available exchange sites and the higher probability of NH_4^+ contacting accessible sites as the solid-to-liquid ratio increases. This dosage dependence is consistent with recent studies using zeolites in real wastewater, where a higher media mass (or bed inventory) enhances overall ammonium capture and delays breakthrough due to greater total exchange capacity [59,60]. The decline in q_e with

increasing dosage is typical in adsorption/ion-exchange systems and is usually attributed to an insufficient concentration of NH_4^+ ions to saturate the greatly increased number of sites, as well as possible particle aggregation and a reduced driving force per gram of adsorbent as the solution is rapidly depleted [61].

3.4. Isotherm Models

The equilibrium adsorption data for $\text{NH}_4^+\text{-N}$ were well described by both the Langmuir and Freundlich isotherm models in their linear and nonlinear forms. Nonlinear Langmuir fitting yielded a very high correlation coefficient, supporting the hypothesis that ammonium uptake by zeolite mainly occurred as monolayer adsorption onto specific exchange sites (Table 2). This observation is consistent with recent wastewater studies using natural clinoptilolite, which also report strong ion-exchange behavior [48]. However, the Freundlich model also showed excellent agreement ($R^2 = 0.9989$), with $1/n < 1$ indicating favorable adsorption. This suggests surface heterogeneity and a non-uniform energy distribution, which is realistic for natural zeolites due to structural defects, varying Si/Al ratios and the presence of multiple cation-exchange sites [62]. According to the chemical composition of the HEU-type zeolite (Si/Al ≈ 4.36) and the presence of exchangeable Ca^{2+} , K^+ , Na^+ and Mg^{2+} cations, a chemically heterogeneous framework with multiple ion-exchange sites is indicated. This structural heterogeneity supports the excellent fit of the Freundlich model, whereas the Langmuir model confirms that NH_4^+ adsorption is predominantly controlled by site-limited ion exchange. Consequently, the comparable fit of both models indicates that ammonium adsorption in this system is predominantly governed by site-limited ion exchange occurring on a heterogeneous surface, in agreement with recent findings in zeolite-based ammonium recovery systems [61].

Table 2. Parameters of the Langmuir and Freundlich isotherm models calculated for $\text{NH}_4^+\text{-N}$ adsorption.

Isotherm Model	Langmuir (Linear)	Langmuir (Nonlinear)
q_m (mg/g)	0.20	0.49
K_L (L/mg)	2.19	0.37
R^2	0.9870	0.9988
Isotherm model:	Freundlich (Linear)	Freundlich (Nonlinear)
K_F (mg/g) (L/mg) $^{1/n}$	0.12	0.13
$1/n$	0.73	0.69
R^2	0.9985	0.9989

3.5. Kinetic Models

Regarding adsorption kinetics, the pseudo-first-order (PFO) and pseudo-second-order (PSO) models were applied to the adsorption data in both linear and nonlinear forms. The PSO model provided an excellent fit ($R^2 = 1.0000$ for the linear form; 0.9891 for the nonlinear form) and, importantly, predicted an equilibrium adsorption capacity ($q_{e,cal} = 0.6218\text{--}0.6232$ mg/g) very close to the experimental value ($q_{e,exp} = 0.6260$ mg/g), as shown in Table 3. In contrast, the linear PFO model performed poorly ($R^2 = 0.6479$) and severely underestimated $q_{e,cal}$ (0.0242 mg/g), indicating that it does not adequately represent the uptake mechanism. Although the nonlinear PFO model improved both R^2 (0.9268) and $q_{e,cal}$ (0.6161 mg/g), its performance remained inferior to that of the PSO model. These results suggest that the adsorption rate is primarily controlled by the availability of active exchange sites and chemisorption-type interactions rather than by simple diffusion

or physical sorption. Recent kinetic investigations have likewise identified the PSO model as the most appropriate for describing ammonium adsorption onto natural and modified zeolites [63,64].

Table 3. Parameters of the PFO and PSO isotherm models for NH_4^+ -N adsorption.

Kinetic Model	Pseudo-First-Order (Linear)	Pseudo-First-Order (Nonlinear)
$q_{e,exp}$ (mg/g)	0.626	0.626
k_1 (1/min)	0.054	1.527
q_e (mg/g)	0.024	0.616
R^2	0.6479	0.9268
Kinetic Model	Pseudo-Second-Order (Linear)	Pseudo-Second-Order (Nonlinear)
k_2 (g/(mg min))	16.126	13.326
q_e (mg/g)	0.622	0.623
R^2	1.0000	0.9891

3.6. Breakthrough Curve

Continuous adsorption experiments for NH_4^+ -N were performed in fixed beds packed with zeolite (80 g) using standard solutions for initial concentrations (C_0) of 15 mg/L, 35 mg/L and 50 mg/L at two different flow rates ($Q = 10$ and 20 mL/min). The breakthrough curves are shown in Figure 6a–f. The comparison of breakthrough curves indicates that the time required to reach both the breakthrough point and the saturation plateau increased as the initial ammonium concentration decreased. Specifically, the breakthrough curve corresponding to the highest influent concentration (50 mg/L) reached breakthrough faster than that obtained at lower concentration (15 mg/L), demonstrating that the slope of the breakthrough curve becomes steeper with increasing influent ammonium concentration. A similar observation has been reported by Gagliano et al. [63] and Zhang et al. [65]. The steeper breakthrough curve observed at a higher inlet ammonium concentration also indicates that a smaller volume of solution is treated before breakthrough occurs [59]. Furthermore, at higher influent concentrations, the greater mass transfer driving force accelerates solute transport within the column, resulting in more rapid saturation of the zeolite bed [28]. Regarding the effect of flow rate, comparison of the breakthrough curves for each initial concentration at the two flow rates showed that a shorter time was required to reach the breakthrough point at the higher flow rate. This behavior is attributed to the reduced contact time between the ammonium ions and the zeolite bed, leading to faster column saturation. Similar observations have been reported in fixed-bed adsorption studies [65,66].

Moreover, two additional continuous adsorption experiments were conducted at $C_0 = 50$ mg/L and $Q = 10$ mL/min using higher zeolite masses (120 g and 160 g), which corresponded to greater bed heights. Comparison of the breakthrough curves revealed that both the breakthrough and saturation times were delayed with the increasing bed height. Specifically, in the case of the longest bed (160 g), the operation time was extended to 9900 min, compared with 4210 min for 80g and 5550 min for 120 g. When the zeolite bed height increases, the mass transfer zone requires more time to travel throughout the column, resulting in a delayed breakthrough time, as also reported by Zhang et al. [65] and Salman et al. [66]. In the present study, the adsorption capacities of 7.50 mg/g, 10.78 mg/g and 14.24 mg/g were gained with increasing bed heights of 80 g, 120 g and 160 g of zeolite, respectively, and the calculated removal efficiencies were ~42.6%, 44.3% and 44.8% correspondingly, while zeolite presented similar behavior as the fixed-bed matrix [66,67].

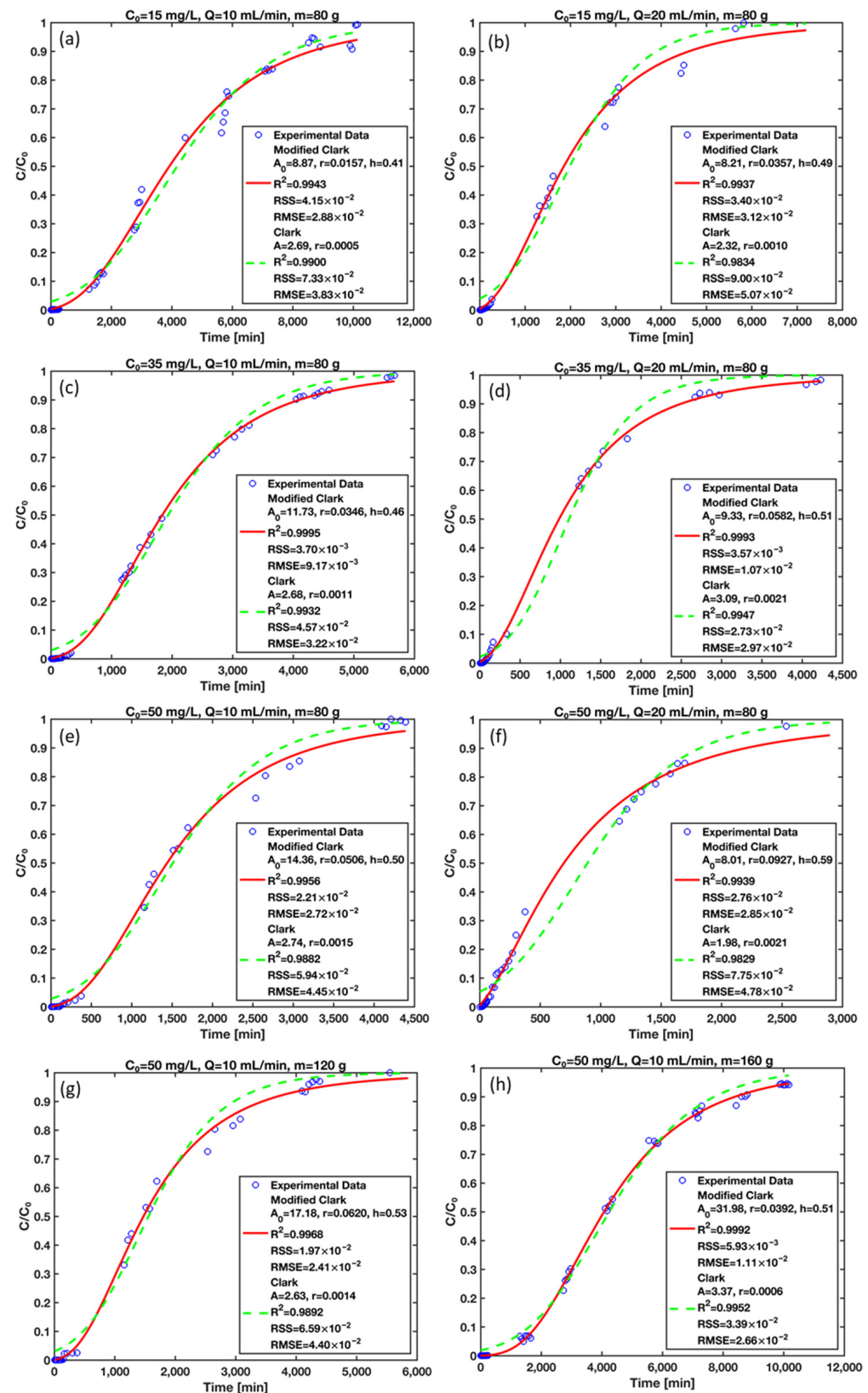


Figure 6. Dimensionless ammonium nitrogen concentration at the outlet of the bed as function of time and fitting curves with Clark and modified Clark models for (a) initial concentration $C_0 = 15 \text{ mg/L}$, $Q = 10 \text{ mL/min}$ and zeolite mass $m = 80 \text{ g}$, (b) $C_0 = 15 \text{ mg/L}$, $Q = 20 \text{ mL/min}$ and $m = 80 \text{ g}$, (c) $C_0 = 35 \text{ mg/L}$, $Q = 10 \text{ mL/min}$ and $m = 80 \text{ g}$, (d) $C_0 = 35 \text{ mg/L}$, $Q = 20 \text{ mL/min}$ and $m = 80 \text{ g}$, (e) $C_0 = 50 \text{ mg/L}$, $Q = 10 \text{ mL/min}$ and $m = 80 \text{ g}$, (f) $C_0 = 50 \text{ mg/L}$, $Q = 20 \text{ mL/min}$ and $m = 80 \text{ g}$, (g) $C_0 = 50 \text{ mg/L}$, $Q = 10 \text{ mL/min}$ and $m = 120 \text{ g}$, (h) $C_0 = 50 \text{ mg/L}$, $Q = 10 \text{ mL/min}$ and $m = 160 \text{ g}$.

The studies summarized in Table 4 demonstrate that natural and synthetic zeolites are effective adsorbents for ammonium removal from both synthetic solutions and landfill leachates, with adsorption capacities strongly influenced by the initial ammonium concentration and wastewater composition. Most studies have focused on batch adsorption using relatively high ammonium concentrations, while fewer investigations have evaluated fixed-bed column performance under continuous-flow conditions. These findings confirm the effectiveness of zeolite-based adsorption and highlight the need for reliable predictive approaches to support process design and optimization.

In all cases, the Thomas kinetic model, Bohart–Adams, Clark, and their modified versions were evaluated to describe the breakthrough data (Table 5), with the modified Clark model providing the better fit (Figure 6).

Table 6 presents the estimated constants of the modified Clark model obtained from the fixed-bed column experiments. The model incorporates the additional parameter h to account for system heterogeneity, allowing a more accurate description of real breakthrough curves [68]. Also, in the present study, Clark's parameter n was fixed and obtained from the Freundlich isotherm, in accordance with the theoretical basis of the Clark model, which combines mass transfer considerations with the Freundlich equilibrium expression. In the literature, increasing the flow rate Q at constant initial concentration, C_0 and bed mass generally results in a steeper breakthrough curve shifted to shorter times. Within the modified Clark framework, this is reflected by an increase in r (rate constant) and a decrease in A (characteristic time), while the additional parameter h accounts for non-idealities such as heterogeneity, channeling, or incomplete initial adsorption [35,36,69]. Experimental results confirm these trends: for $C_0 = 15$ mg/L and the 80 g bed, r increased from 0.0157 to 0.0357 and A decreased from 8.87 to 8.21 as Q increased from 10 to 20 mL/min; similar trends were observed for C_0 35 mg/L and 50 mg/L. These results indicate that higher flow rates accelerate breakthrough and steepen the curves, while h allows the model to capture the initial portion of the curves where deviations from zero occur. Similarly, increasing C_0 at a constant Q and bed mass accelerates bed exhaustion, enhancing mass transfer. This is typically reflected by increases in both r and A , with h capturing deviations from ideal column behavior. For $Q = 10$ mL/min and a bed mass of 80 g, r increased from 0.0157 to 0.0346 to 0.0506 and A increased from 8.87 to 11.73 to 14.36 as C_0 increased from 15 to 35 to 50 mg/L, indicating faster breakthrough and steeper curves at higher concentrations, consistent with the literature [36]. Increasing the bed mass (or height) at a constant C_0 and Q generally prolongs breakthrough, increasing A and often decreasing r due to the larger mass transfer zone. Again, h accounts for non-idealities that may distort these trends [70]. For $C_0 = 50$ mg/L and $Q = 10$ mL/min, as bed mass increased from 80 → 120 → 160 g, A increased from 14.36 to 17.18 and finally to 31.98, while r initially increased slightly (from 0.0506 to 0.0620) likely due to local hydrodynamic effects and then decreased (0.0392) at 160 g, reflecting the prolonged breakthrough times associated with a larger mass transfer zone. This minor deviation, such as the slight increase in r in the case of the 120 g bed, is consistent with practical column effects like channeling or uneven site accessibility. The h parameter allowed the model to accurately fit the non-ideal behavior in taller beds, improving predictive capability of the fit. Furthermore, it is reported that the effect of the adsorbent's mass on the Clark parameters is not linear but may vary under specific operating conditions, suggesting that more experiments are requested to predict in detail the behavior of the parameter r [71].

Table 4. Comparison of recent studies on ammonium removal by zeolite adsorption.

Adsorbent	Wastewater	NH ₄ ⁺ -N (mg L ⁻¹)	Batch/Column	Max Removal (%)	Max Adsorption Capacity (mg g ⁻¹)/ Initial NH ₄ ⁺ -N (mg L ⁻¹)	Best Isotherm	Best Kinetic/Breakthrough Model	Ref.
Natural Gördes clinoptilolite	Real landfill leachate	200–3750	Batch	> 80.0	20.37/3750	-	-	Karadag et al. [28]
Natural Gördes clinoptilolite	Real landfill leachate	100–400	Column	>90.0	16.32/200	-	Thomas	
Natural Gördes clinoptilolite	Real landfill leachate	194–3750	Column	~90.0	6.78/200	-	Clark	Karadag et al. [29]
Natural clinoptilolite	Real landfill leachate	75–2805	Batch	51.8	9.13/2805	Langmuir	-	Vollprecht et al., [31]
Natural Gördes zeolite	Real landfill leachate	263–1364	Batch	92.5	~ 8.4/1364	Langmuir–Tempkin	PSO *	Aydin Temel & Kuleyin [27]
Natural clinoptilolite	Mature landfill leachate	100–600	Batch	51.6	3.59/600	Temkin	PSO *	Genethliou et al. [42]
Synthetic zeolite	Synthetic wastewater	10–100	Batch	~34.0	18.35	Freundlich	-	Gagliano et al. [63]
		10 or 40	Column	~60.0	3.6/40	-	Dose–response model	
HEU-zeolite	Synthetic solution	5–35	Batch	96.5	0.62/model	Freundlich	PSO	
	RO-treated real landfill leachate	35	Batch	94.0	2.56			Present study
	Synthetic solution	15–50	Column	-	14.24	-	Modified Clark	

* PSO: Pseudo-second order kinetic model.

Table 5. Statistical parameters (R² and RMSE) for the evaluated kinetic models.

Exp. Number	Initial Concentration C ₀ (mg/L)	Flow Rate Q (mL/min)	Zeolite Mass, m (g)	Thomas Model/ Modified Thomas Model	Bohart–Adams Model/ Modified Bohart–Adams Model		Clark Model/ Modified Clark Model		
				R ²	RMSE	R ²	RMSE	R ²	RMSE
1	15	10	80	$9.82 \cdot 10^{-1} / 9.94 \cdot 10^{-1}$	$7.62 \cdot 10^{-1} / 3.09 \cdot 10^{-2}$	$8.30 \cdot 10^{-1} / 9.94 \cdot 10^{-1}$	$2.37 \cdot 10^0 / 2.96 \cdot 10^{-2}$	$9.90 \cdot 10^{-1} / 9.94 \cdot 10^{-1}$	$3.83 \cdot 10^{-2} / 2.88 \cdot 10^{-2}$
2	15	20	80	$9.72 \cdot 10^{-1} / 9.94 \cdot 10^{-1}$	$9.87 \cdot 10^{-1} / 3.15 \cdot 10^{-2}$	$7.40 \cdot 10^{-1} / 9.94 \cdot 10^{-1}$	$3.02 \cdot 10^0 / 3.17 \cdot 10^{-2}$	$9.83 \cdot 10^{-1} / 9.94 \cdot 10^{-1}$	$5.07 \cdot 10^{-2} / 3.12 \cdot 10^{-2}$
3	35	10	80	$9.84 \cdot 10^{-1} / 2.24 \cdot 10^{-1}$	$1.74 \cdot 10^0 / 3.45 \cdot 10^{-1}$	$7.94 \cdot 10^{-1} / 9.99 \cdot 10^{-1}$	$6.23 \cdot 10^0 / 8.50 \cdot 10^{-3}$	$9.93 \cdot 10^{-1} / 9.99 \cdot 10^{-1}$	$3.22 \cdot 10^{-2} / 9.17 \cdot 10^{-3}$
4	35	20	80	$9.91 \cdot 10^{-1} / 8.75 \cdot 10^{-1}$	$1.40 \cdot 10^0 / 1.45 \cdot 10^{-1}$	$6.82 \cdot 10^{-1} / 9.99 \cdot 10^{-1}$	$8.09 \cdot 10^0 / 1.16 \cdot 10^{-2}$	$9.95 \cdot 10^{-1} / 9.99 \cdot 10^{-1}$	$2.97 \cdot 10^{-2} / 1.07 \cdot 10^{-2}$
5	50	10	80	$9.78 \cdot 10^{-1} / 7.78 \cdot 10^{-1}$	$3.06 \cdot 10^0 / 1.93 \cdot 10^{-1}$	$8.23 \cdot 10^{-1} / 9.96 \cdot 10^{-1}$	$8.60 \cdot 10^0 / 2.69 \cdot 10^{-2}$	$9.89 \cdot 10^{-1} / 9.96 \cdot 10^{-1}$	$4.45 \cdot 10^{-2} / 2.72 \cdot 10^{-2}$

Table 5. Cont.

Exp. Number	Initial Concentration C ₀ (mg/L)	Flow Rate Q (mL/min)	Zeolite Mass, m (g)	Thomas Model/ Modified Thomas Model	Bohart–Adams Model/ Modified Bohart–Adams Model	Clark Model/ Modified Clark Model			
6	50	20	80	$9.77 \cdot 10^{-1} /$ $0.19 \cdot 10^{-1}$	$2.74 \cdot 10^0 /$ $3.61 \cdot 10^{-1}$	$7.35 \cdot 10^{-1} /$ $9.96 \cdot 10^{-1}$	$8.60 \cdot 10^0 /$ $2.39 \cdot 10^{-2}$	$9.83 \cdot 10^{-1} /$ $9.94 \cdot 10^{-1}$	$4.78 \cdot 10^{-2} /$ $2.85 \cdot 10^{-2} /$
7	50	10	120	$9.80 \cdot 10^{-1} /$ $7.95 \cdot 10^{-1}$	$3.01 \cdot 10^0 /$ $1.92 \cdot 10^{-1}$	$7.50 \cdot 10^{-1} /$ $9.97 \cdot 10^{-1}$	$10.59 \cdot 10^0 /$ $2.39 \cdot 10^{-2}$	$9.90 \cdot 10^{-1} /$ $9.97 \cdot 10^{-1}$	$4.40 \cdot 10^{-2} /$ $2.41 \cdot 10^{-2} /$
8	50	10	160	$9.90 \cdot 10^{-1} /$ $2.49 \cdot 10^{-1}$	$2.12 \cdot 10^0 /$ $3.12 \cdot 10^{-1}$	$8.22 \cdot 10^{-1} /$ $9.99 \cdot 10^{-1}$	$8.08 \cdot 10^0 /$ $1.11 \cdot 10^{-2}$	$9.95 \cdot 10^{-1} /$ $9.99 \cdot 10^{-1}$	$2.66 \cdot 10^{-2} /$ $1.11 \cdot 10^{-2} /$

Table 6. Experimental conditions of the fitted experiments: initial ammonium nitrogen concentration, flow rate and zeolite mass, and the predicted constants of the modified Clark's model ($n = 1.37$ for all experiments).

Experiment Number	Initial Concentration C_0 (mg/L)	Flow Rate Q (mL/min)	Zeolite Mass, m (g)	A	r (1/min)	h
1	15	10	80	8.87	0.0157	0.41
2	15	20	80	8.21	0.0357	0.49
3	35	10	80	11.73	0.0346	0.46
4	35	20	80	9.33	0.0582	0.51
5	50	10	80	14.36	0.0506	0.50
6	50	20	80	8.01	0.0927	0.59
7	50	10	120	17.18	0.0620	0.53
8	50	10	160	31.98	0.0392	0.51

Overall, the modified Clark model successfully described ammonium adsorption dynamics in fixed-bed zeolite columns and provided a reliable framework for design and scale-up of continuous-flow adsorption systems.

3.7. Development of a Global Fitting Algorithm with Shared Parameters

The experimental study allowed the estimation of the constants A , r , and h of the modified Clark model under different operating conditions in fixed-bed adsorption columns. While experimental results were reliable and comprehensive, their use in new operating scenarios (e.g., different influent concentrations or zeolite masses) would necessitate further time-consuming and costly experiments. Therefore, a predictive modeling methodology was developed to correlate the model constants with the main operating parameters (C_0 , Q and zeolite mass), creating an algorithm capable for the estimation of system performance without the need for a large number of new experimental trials at laboratory scale. This approach also enhances understanding of the effect of operating variables on model parameters, which is essential for process optimization and scale-up.

Recent studies have applied modeling approaches to describe ammonium adsorption onto zeolites. Yolcu et al. [72] developed hybrid predictive models combining response surface methodology (RSM) and artificial neural networks (ANNs) to estimate ammonium removal under varying operational conditions. Similarly, Aydın Temel et al. [73] employed multilayer perceptron neural networks (MLP) to model adsorption performance and optimize prediction accuracy. These studies focus on data-driven predictive frameworks for estimating adsorption behavior. The present work adopts an alternative strategy by formulating explicit mathematical relationships between A and r as functions of the initial concentration (C_0), flow rate (Q), and zeolite mass, while systematically evaluating multiple functional forms (polynomial, exponential-linear, log-linear and log-log). Model selection is based on statistical criteria (R^2 , RMSE and validation deviation) and parameter estimation through nonlinear optimization (MATLAB fminsearch), providing a structured analytical modelling framework.

The dataset, comprising eight experiments, was divided into two subsets: a training set, comprising five experiments (experiments 1, 2, 5, 6 and 8, Table 3), which was used for developing and calibrating the equation; and a validation set (experiments 3, 4 and 7, Table 5), comprising three experiments, which was used to evaluate the predictive capability. The validation set included intermediate operating conditions ($C_0 = 35$ mg/L and zeolite mass of 120 g) to provide a challenging test of the model's ability to generalize. Accurate prediction of these intermediate cases indicates robustness within the experimental design space.

The algorithm-derived model was selected based on three criteria: the coefficient of determination (R^2), the root mean square error ($RMSE$) and the deviation from the validation dataset. Parameter estimation was performed using the `fminsearch` function in MATLAB. While the second-degree polynomial yielded slightly higher R^2 values and a lower $RMSE$ (Table 7), the exponential–linear formulation was chosen because it offered the best balance of simplicity, accuracy and predictive performance with minimal validation error. No predictive equation was developed for h (which introduces the effect of heterogeneity into modified Clark’s model), as its experimental variation was limited, so it was fixed at its average value. The emphasis was placed on A and r , as these primarily determine the quantitative breakthrough behavior.

Table 7. Coefficient of determination (R^2) and root mean square error ($RMSE$) for the functional forms evaluated.

	R^2		$RMSE$	
	A	r	A	r
Polynomial (2nd degree)	0.98133	0.99072	1.03089	0.002086
Exponential–Linear	0.96448	0.92771	1.42184	0.005824
Log–Linear	0.94187	0.90550	1.81895	0.006659
Log–Log	0.93603	0.89095	1.90820	0.007153

The equations that described constants A and r with the exponential–linear formulation were as follows:

$$A(C_0, Q, m) = \exp(0.0065C_0 - 0.0330Q + 0.0116m + 1.6150) \quad (18)$$

$$R^2 = 0.9845 \text{ and } RMSE = 1.1376$$

$$r(C_0, Q, m) = \exp(0.0303C_0 + 0.0712Q - 0.0025m - 5.0626) \quad (19)$$

$$R^2 = 0.9886 \text{ and } RMSE = 0.0027$$

while h was considered constant:

$$h = \text{const} = h_{\text{mean}} = 0.49933$$

The surface plots of A as a function of the flow rate and initial ammonium nitrogen concentration showed that it increases with increasing initial concentration and decreasing flow rate. In contrast, the values of the r constant increased with both increasing initial ammonium nitrogen concentration and increasing flow rate (Figure 7).

The predictive performance of the selected model is summarized in Table 8. In two of the three validation experiments, deviations between predicted and experimental values were small, confirming satisfactory predictive capability. In the third case ($C_0 = 50 \text{ mg/L}$, $m = 120 \text{ g}$), the deviation in r values was higher, consistent with the previously discussed experimental anomaly, where r increased instead of decreasing with bed mass. This behavior likely reflects nonlinear hydrodynamic or mass transfer effects that require further investigation.

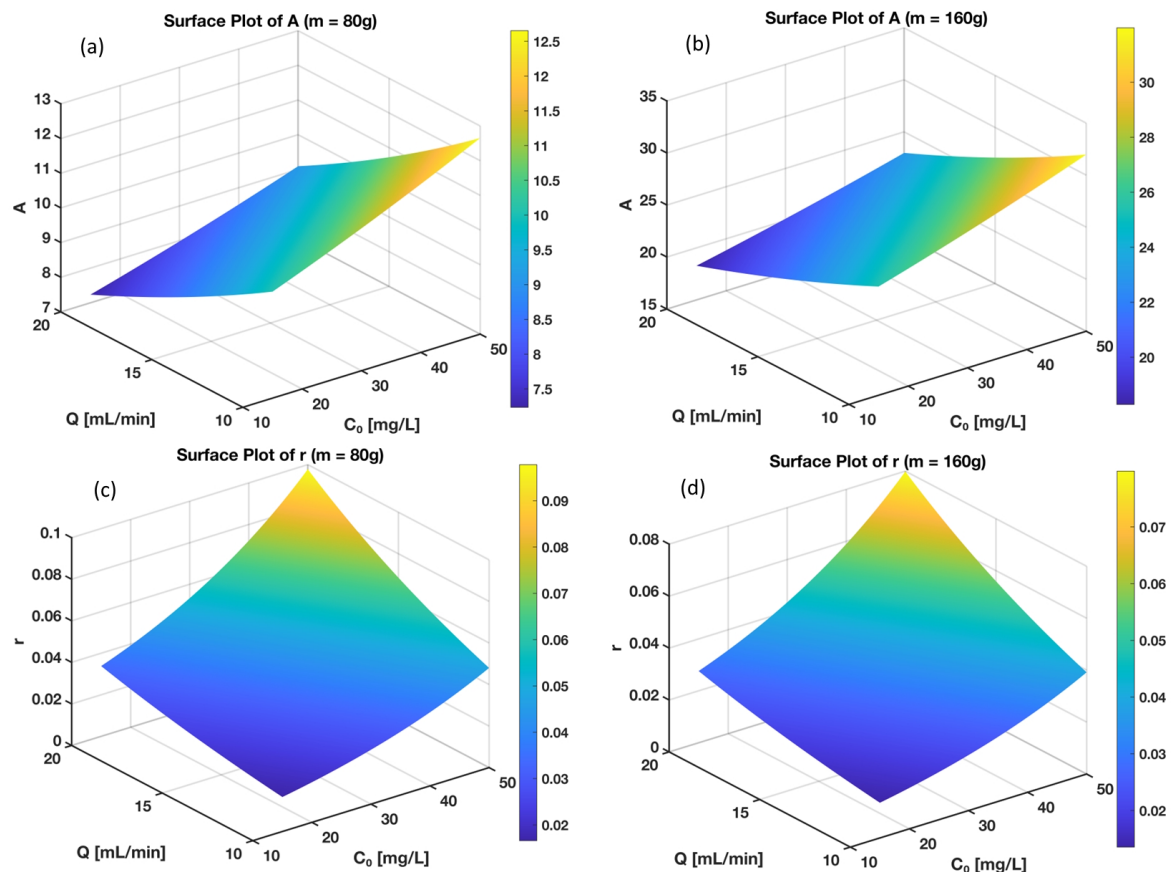


Figure 7. Surface plots for A and r value constants; surface plots of A as function of flow rate and ammonium nitrogen initial concentration for zeolite mass (a) $m = 80$ g and (b) $m = 160$ g; surface plots of r as a function of flow rate and ammonium nitrogen initial concentration for zeolite mass (c) $m = 80$ g and (d) $m = 160$ g.

Table 8. Results obtained using the developed algorithm under various experimental conditions and comparison with experimental data. “REAL” refers to values calculated from experimental data, whereas “PRED” refers to predicted values.

C_0 (mg/L)	Q (mL/min)	m (g)	A_{REAL}	A_{PRED}	Error (%)	RMSE	r_{REAL} (1/min)	r_{PRED} (1/min)	Error (%)	RMSE
35	10	80	11.73	11.47	2.15	0.25	0.035	0.031	11.90	0.004
35	20	80	9.33	8.24	11.63	1.09	0.058	0.062	6.53	0.004
50	10	120	17.18	20.12	17.08	2.93	0.062	0.043	30.10	0.018

Recent developments in adsorption modeling have increasingly focused on linking isotherm or kinetic parameters to experimental conditions. Pereira et al. [74] introduced a modified Langmuir–Freundlich isotherm in which the affinity constant is explicitly expressed as a function of solution pH, demonstrating that model parameters can be treated as dependent variables rather than fixed constants. Similarly, Danat et al. [75] reviewed a broad range of adsorption isotherm models and emphasized the growing use of non-linear regression and advanced fitting methodologies to determine model parameters more accurately across diverse adsorption systems. Also, some studies express adsorption constants (e.g., K_L) as functions of temperature using Arrhenius-type equations. Thus, model parameters vary with temperature instead of remaining fixed [76]. Building on these concepts, the present work formulates the adsorption parameter A as a function of the initial concentration (C_0), flow rate (Q), and zeolite mass (m) using an exponential–linear

relationship. This approach allows the constants A and r to adapt to experimental conditions while maintaining analytical transparency, with model selection guided by statistical criteria (R^2 , $RMSE$, and validation deviation) and parameter estimation performed via nonlinear optimization in MATLAB.

Overall, the developed prediction code represents a significant step toward quantitative modeling of ammonium adsorption in fixed-bed zeolite columns. The methodology successfully formulates equations for A and r , demonstrates reliable prediction within the experimental domain, and identifies cases where additional experimental refinement may be required. Importantly, the developed algorithm reduces the need for new experiments, supports process understanding through parameter–constant relationships and provides a foundation for future extensions, such as incorporation of additional variables (e.g., temperature or competing ions) or implementation of advanced modeling techniques (e.g., machine learning approaches).

4. Conclusions

In this study, batch and continuous-flow experiments were performed to investigate the adsorption of NH_4^+ -N on zeolite using both standard solutions and landfill leachates. The experimental data obtained from batch reactors showed that increasing the zeolite mass enhanced NH_4^+ -N removal, whereas higher initial NH_4^+ -N concentrations reduced adsorption efficiency and increased the adsorption capacity, as can be explained from the equations used. Nevertheless, high removal efficiencies were achieved even at high initial NH_4^+ -N.

The batch experimental data were fitted using kinetic and isothermal models. The PSO model provided the better fit for the kinetic data, indicating that chemisorption predominated during the experiments. The Freundlich isotherm adequately described the equilibrium data, suggesting a heterogeneous adsorption process. These findings were consistent with results obtained from fixed-bed column experiments under continuous-flow conditions, where breakthrough curves were successfully fitted with dynamic adsorption models.

Among the kinetic models applied to the continuous-flow experiments, the modified Clark model provided the best fit, in agreement with the Freundlich behavior observed in the batch experiments. Empirical equations were developed to relate the model constants to operational parameters using training and validation datasets, achieving satisfactory predictive accuracy. The results of this study demonstrate the effectiveness of raw zeolite application as an RO effluent post-treatment adsorbent for NH_4^+ -N removal, while based on the experimental data a practical tool for process prediction and scale-up was obtained.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/su18147278/s1>, Figure S1: Schematic diagram of (a) batch and (b) column system.; Figure S2: Effect of pH on NH_4^+ -N removal as function of time.

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Abbreviations

The following abbreviations are used in this manuscript:

RO	Reverse osmosis
LL	Landfill leachate
SS	Synthetic solutions
DW	Deionized water
SSA	Specific surface area
RMSE	Root mean square error
PFO	Pseudo-first-order kinetic model
PSO	Pseudo-second-order
RSM	Response surface methodology

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