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Zeolites for Nitrogen Recovery from the Anaerobic Membrane Bioreactor Permeate: Zeolite Characterization

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Abstract: Anaerobic Membrane Bioreactor technology has great advantages for treating wastewater, including energy recovery from organic matter. However, when the legislation requires that effluent standards be met in sensitive areas, this treatment cannot remove the nutrients, thus the permeate generated needs post-treatment. Apart from the biological processes, ion exchange is an alternative treatment for this stream since it can remove nutrients and concentrate them for later recovery as fertilizers. In this work, the feasibility of using a natural zeolite (clinoptilolite) for treating NH₄ from AnMBR permeate was studied and tests were carried out on the adsorption kinetics of ammonium. Isotherm tests verified that activating natural zeolite to its -Na form improves its performance by 20% and increases q_e from 2.37 to 2.86 mg NH₄-N/g for a Co of 30 mg NH₄-N/L. It was also found that the cations present in the water (especially Ca²⁺ and Na⁺) caused a 22% reduction in ammonium adsorption while organic matter was responsible for improving the retained ammonium by 22%. It was also found that the working pH (7.2 ± 0.2) is close to the optimal pH range (6–7) for zeolite performance. The tests on the AnMBR permeate indicate that clinoptilolite is a suitable material since treating this stream can retain up to 7.44 mg NH₄-N/g.



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1. Introduction

Traditionally, wastewater treatment has only focused on the correct removal of pollutants in accordance with the current legislation. However, the growing pressure on water resources and the emergence of new treatment alternatives that can recover nutrients from water, plus the need to reduce energy consumption (and therefore the environmental impact) in Wastewater Treatment Plants (WWTPs) has given rise to a new concept involving the so-called resource recovery facilities. In this scenario of continuous technological evolution towards a sustainable treatment within the concept of the circular economy, Anaerobic Membrane Bioreactors (AnMBR) have become an alternative to the conventional process. AnMBR technology offers the advantages of the anaerobic treatment of organic matter due to its low energy consumption and the possibility of energetically valorizing the organic matter from the mainstream. Anaerobic processes also remove few of the nutrients and ammonification takes place under anaerobic conditions, so that an effluent with a high nutrient concentration is obtained [1]. High nutrient concentrations together with the absence of solids and pathogenic organisms due to the use of ultrafiltration membranes to retain the biomass generate water suitable for use in irrigation. However, when nutrient removal is required to meet the discharge requirements in a sensitive area the nutrients have to be removed in a post-treatment.

Different treatment systems for this permeate have already been proposed, e.g., Lee and Liao [2] suggested a classic process of nitrification and denitrification using the CH₄ generated in the anaerobic stage. Kong et al. [3] proposed coupling a partial nitrification

process and Anammox to eliminate nitrogen without the need for a carbon input. However, these solutions focus on nutrient removal rather than nutrient recovery, as has been pointed out by different authors [4]. These authors used a microalgae photobioreactor for the post-treatment of the AnMBR permeate to concentrate the nutrients in the biomass for later recovery. Deng et al. [5] and C. Liu et al. [6] proposed the ion exchange (IEX) process as a mechanism for the concentration of nutrients through adsorption, followed by their release and post-treatment to recover ammonium and phosphorus.

Initially, the IEX process was not widely used to treat municipal wastewater due to a series of disadvantages, such as clogging the adsorbent surface, the low selectivity of the medium or the cost of regeneration [7]. The growing use of membrane technologies in wastewater treatment to generate permeates free of suspended solids, and the recent research on the capacity of different media and how to operate them have allowed the IEX process to become an alternative for the recovery of nutrients due to its ease of operation, low cost and good performance [6].

As the adsorption process is influenced by all the ions present in the water stream under treatment, when choosing an adsorbent the affinity of the material for the target ion has to be taken into account. In the case of ammonium, it has been shown that the cations due to the hardness of the water (such as calcium or magnesium) [8] play an important role in determining the type of adsorbent to use and the loss of performance due to the competition between the cations that are not of interest. Although strong acid cationic resins (SAC) usually have high adsorption values [9], in very hard water, these materials tend to offer worse performance due to their greater affinity for the divalent cations. Gong et al. [9] indicated that due to the interference of divalent cations, it was only possible to retain and concentrate 37.5% of the ammonium present in the water with SAC while Wang et al. [10], working with zeolites, observed only a 10% capacity loss for these same reasons. Under these conditions, it is more appropriate to work with natural zeolites (N-Z) since, although N-Z does not reach these high yields in the absence of the interferents of SAC, under actual working conditions, N-Z offer better ammonium retention capacity [9,11].

In the present study, an experimental procedure has been proposed in order to select the adsorbent material most selective to the AnMBR permeate and to assess the effect over the ammonium retention capacity of different adsorbent properties and the presence of different components. Through a kinetic study, the affinity of the proposed materials was evaluated. Subsequently, through a set of isotherm tests, the natural zeolite was characterized, and it was analyzed how nitrogen adsorption efficiency is affected by different variables (particle size and zeolite activation process) and other variables that are dependent on real water characteristics (pH, organic matter, ions present).

2. Materials and Methods

2.1. Materials

Two types of adsorbents were used for the study: natural zeolite and ion exchange resin. The zeolite was a clinoptilolite supplied by Zeocem. Clinoptilolite has a higher affinity for monovalent than divalent cations ($\text{Cs}^+ > \text{NH}_4^+ > \text{Pb}^{2+} > \text{K}^+ > \text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Ba}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$). Particles between 500 and 1000 μm were used for isotherms and kinetic experiments according to the preliminary tests while natural zeolite (N-Z) was submerged and slowly stirred in a NaOH 1M solution for 1 h to convert it to the Na form (Na-Z). After one hour of contact, the zeolite was washed with deionized water, and the pH was reduced to 7 by stripping with CO_2 , which considerably reduced the water consumption for washing the zeolite and bringing it up to the working pH, which is one of the bottlenecks in the zeolite activation process. Purolite SSTC60, a strong acid cation exchange resin (SAC), was also studied. Unlike zeolites, resins have a higher affinity for divalent cations than for ammonium, so it is possible that interferences with the hardness of the water will be detected [11]. Resins are provided with a similar particle size to the zeolite (300–1200 μm) and in Na- form so that previous activation is not needed.

Preliminary kinetics studies were carried out on the AnMBR permeate to determine the minimum contact time for the isotherm test and the adsorbent that provided the highest ammonium adsorption capacity working with the wastewater used. A description of the permeate is shown in Table 1.

Table 1. Characterization of the different solutions used for adsorption kinetics and isotherms.

Influent	Deionized Water	Tap Water	AnMBR Permeate
Ca ²⁺ (mg Ca ²⁺ /L)	N.D.	116	119
Mg ²⁺ (mg Mg ²⁺ /L)	N.D.	29.7	32.3
Na ⁺ (mg Na ⁺ /L)	0.16	287	109
K ⁺ (mg K ⁺ /L)	N.D.	12.1	14.4
NH ₄ ⁺ (mg NH ₄ ⁺ -N/L)	N.D.	N.D.	28.8
Cl ⁻ (mg Cl ⁻ /L)	2.2	122.8	194
NO ₃ ⁻ (mg NO ₃ ⁻ -N/L)	N.D.	N.D.	N.D.
PO ₄ ³⁻ (mg PO ₄ ³⁻ -P/L)	N.D.	N.D.	3.3
mg COD/L	N.D.	N.D.	68.2
mg BOD/L	N.D.	N.D.	19.5
pH	7.6	7.3	7.2

Note(s): N.D. = not detected.

Isotherm experiments were conducted on different solutions:

- Prepared ammonium aqueous solutions with deionized water and NH₄Cl
- Tap water fortified with NH₄Cl
- Tap water fortified with NH₄Cl and enriched with PO₄ at the same concentration found in the AnMBR permeate
- Tap water fortified with NH₄Cl and with organic components (glucose and methanol) to study the effect of organic matter.
- Permeate of AnMBR process.

Details of the solutions are given in Table 1. Solutions b, c, and d have the same matrix and only differ in the compounds added to study their interference.

2.2. Kinetic Batch Sorption Studies

Kinetic tests were carried out to fix the minimum time of contact in batch studies and determine the different zeolite and resin responses under the same conditions. These tests were performed in duplicate at room temperature (20 °C), and pH was fixed by Na₂CO₃ to adjust the values to around 7.2 ± 0.2, similar to that in the AnMBR permeate. The zeolite N-Z form was used. The adsorbent concentration was kept similar in both adsorbents: 1g of dry adsorbent in 200 mL of AnMBR permeate. The adsorbents were stirred at 200 rpm in an orbital stirrer for up to 48 h. Each test was made up of 12 samples measured at different times. A sample was prepared for each time to keep the adsorbent concentration constant at all times since at least 5 mL of solution was required to measure the ammonium.

The ammonium adsorption capacity was calculated by Equation (1):

$$q_e = (C_o - C_e) \frac{V}{w} \quad (1)$$

where q_e is the amount of ammonium in the solid phase (mg/g) at time t ; C_o (mg/L) and C_e (mg/L) represent the initial and equilibrium ammonium concentration, respectively; V (L) is the volume of the chosen solution; and w (g) is the mass of adsorbent employed.

The kinetic experiments were fitted to two mathematical models to determine the best fit. A pseudo first-order (PFO) kinetic equation is given by the relationship Equation (2):

$$q_t = q_{th}(1 - \exp(-k_1 t)) \quad (2)$$

where q_t (mg/g) and q_{th} (mg/g) are the experimental adsorption capacity at time t and the theoretical adsorption capacity, respectively; k_1 is the rate constant of the PFO kinetics

model (1/min), and t is the time (min). If the rate of ammonia adsorption follows first-order behaviour, a plot of $\ln(q_{th} - q_t)$ vs. t should follow a linear regression in which the slope is $-k_1$ and intercept $\ln q_{th}$.

A pseudo-second-order (PSO) kinetic model was also used to describe the behaviour of the kinetics as in Equation (3):

$$q_t = \frac{k_2 q_{th}^2 t}{1 + k_2 q_{th} t} \quad (3)$$

where k_2 is the rate constant of the PSO kinetics model (g/mg min). If PSO behaviour is followed, a plot of t/q_t vs. t should yield a straight line with slope $1/k_2 q_{th}^2$ and intercept $1/q_{th}$.

The ability of both models to fit the experimental data was evaluated by calculating the mean root mean squared error (RMSE) Equation (4):

$$RMSE = \sqrt{\frac{1}{N-2} \sum_{i=1}^N (q_{exp,i} - q_{eth,i})^2} \quad (4)$$

where N is the sample size, $q_{exp,i}$ is the experimental value of q_e of the sample i and $q_{eth,i}$ is the value of q_e obtained using the model in the same conditions as $q_{exp,i}$.

2.3. Equilibrium Studies

The first batch of isothermal tests was carried out to determine the importance of previously activating zeolites and the behaviour of the zeolites in relation to the main types of possible interference with the working water used: cations, phosphorus, and organic matter. These batch equilibrium sorption tests were carried out keeping the zeolite concentration at: 1.0 g of dry N-Z or Na-Z was equilibrated with 200 mL of the chosen solution. All the experiments were performed under similar conditions to the kinetic test: in duplicate at room temperature (20 °C), pH fixed at 7.2. The zeolites were stirred at 200 rpm in an orbital shaker for four hours of time contact, according to the kinetic results. A range of ammonium concentration was selected between 10–70 mg NH₄-N/L, considering the average ammonium value in the AnMBR permeate treatment. To prepare these concentrations, real AnMBR permeate was diluted with tap water to achieve the lowest concentration and fortified with NH₄Cl for the highest concentrations. A sample of 5 mL was collected for NH₄-N analysis after being filtered.

Adsorption equilibrium of ammonium was evaluated according to the Langmuir and Freundlich isotherms. This model is the most commonly used in isotherm studies, so more data can be obtained from other studies to compare with our results. The Langmuir isotherm is as in Equation (5):

$$q_e = \frac{q_{max} k_L C_e}{1 + k_L C_e} \quad (5)$$

where q_{max} (mg/g) is the maximum sorption capacity and K_L (L/mg) is the Langmuir constant of the free energy of adsorption. Plotting C_e/q_e versus C_e should follow a linear regression where the slope is $1/q_{max}$ and intercept $1/q_{max} \cdot K_L$.

The Freundlich isotherm is defined by Equation (6):

$$q_e = k_f C_e^{1/n} \quad (6)$$

where k_f ((mg/g) · (L/mg)^{1/n}) is the Freundlich adsorption capacity constant and n is the Freundlich constant of the adsorption intensity (dimensionless). If adsorption follows Freundlich behaviour, a plot of $\ln q_e$ vs. $\ln C_e$ should yield a straight line of which $1/n$ is the slope and $\ln k_f$ the intercept.

RMSE Equation (4) was also applied to find the model that best fitted the experimental data.

The second batch of tests was carried out in the same way as in the previous isotherms to determine the influence of pH on the adsorption process with this type of zeolite. In this case only permeate from the AnMBR process was used and the pH was adjusted from 4 to 9 using HCl 0.1M and NaOH 1M.

3. Results and Discussion

3.1. Adsorption Kinetics

The ammonium sorption kinetic data for N-Z are similar to those of the conventional zeolite behaviour described in other studies (Figure 1). In the first 20 min, ammonium adsorption reached 50%; after that fast step, the ammonium removal rate dropped, indicating that particle diffusion controls the sorption rate process, as has been observed in previous studies [12–14]. An amount of 90% ammonium adsorption was reached after 3 h, and after 4 h, the increase in ammonium removal was negligible, indicating equilibrium has been reached. These values are consistent with those reported in the literature since many researchers have emphasized that after a 2–4 h contact time equilibrium can be assumed [15–17]. The kinetic data was fitted to two Kinetic equation models: pseudo-first order (PFO) and pseudo-second order kinetic (PSO) (Figure 1). The calibration parameter values of both models are listed in Table 2. According to RMSE, PFO kinetics are not able to reproduce the experimental values observed while PSO kinetic represent the kinetic data with a low error. This behaviour is commonly found in the bibliography [11,18,19] and confirms that the PSO model is more consistent since adsorption capacity governs the adsorption rate and is not the adsorbate concentration [20]. Ammonium adsorption takes place in three phases: first of all, ammonium is diffused from the liquid phase to a liquid–solid interface, after which the ammonium in the liquid–solid interface moves to a solid surface, and finally, ions diffuse into the particle pores [16]. Since the batch kinetics tests were carried out under continuous stirring, the ammonium diffusion rate from the aqueous phase is quite high while intraparticle diffusion forms the main bottleneck. These different rates explain why adsorption is fast in the early stages and then drops drastically.

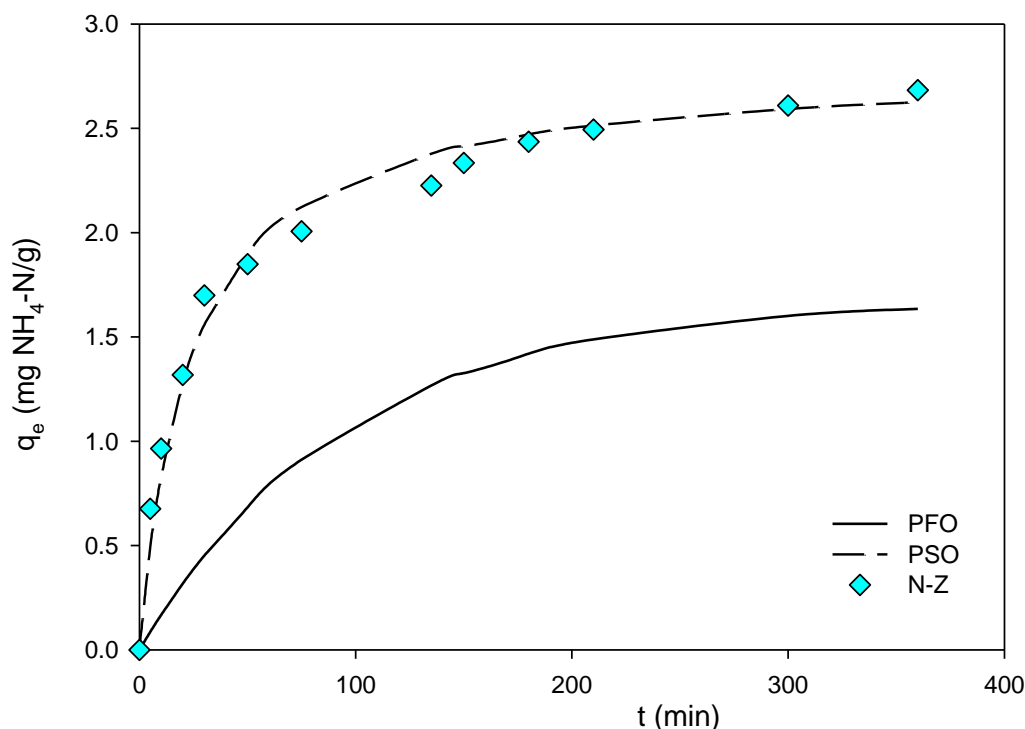
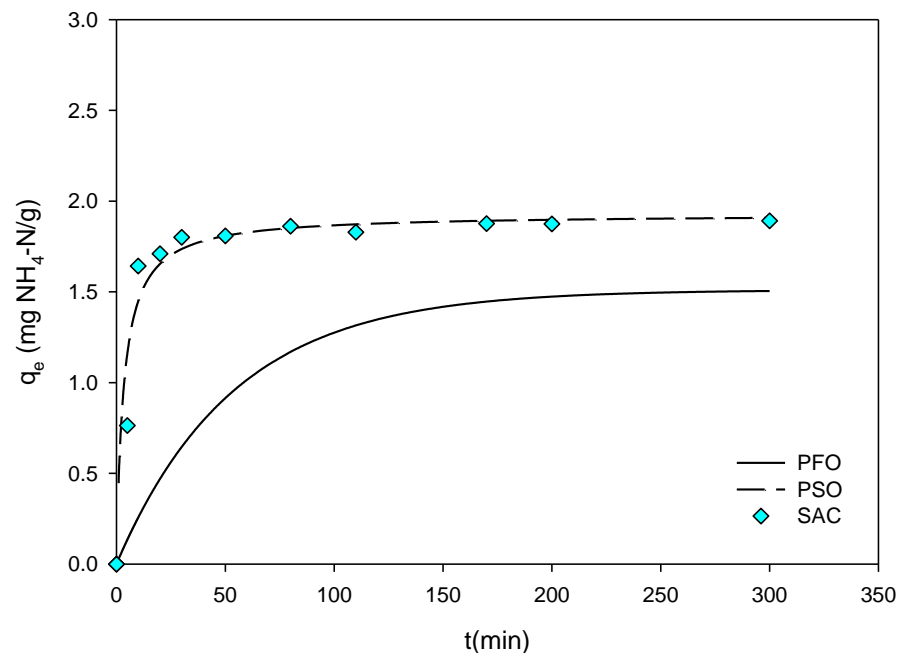


Figure 1. Pseudo-first- and pseudo-second-order kinetics of AnMBR permeate with N-Z.

Table 2. Kinetic parameters for ammonium removal by N-Z and Purolite SSTC60.

		K	q_{eth}	q_{exp}	RMSE
PFO	N-Z	0.0105	1.67	2.68	1.11
	Purolite SSTC60	0.1086	1.51	1.925	0.89
PSO	N-Z	0.0149	2.80	2.68	0.11
	Purolite SSTC60	0.1559	1.93	1.92	0.07

Figure 2 shows the result of the kinetic test working with Purolite SSTC60 resin. The data show a better fit with the PSO model, as with N-Z, as both experiments were performed under the same conditions. The same conclusions can be applied to both fit models with the observed data. SAC tend to show a faster response to remove nitrogen than N-Z as evidenced by the results obtained by other authors [11,21]. The high rate of ammonium adsorption should be noted, which reached 85% maximum capacity in only 10 min due to Purolite SSTC60 has inert core. Adsorption took place in the layers nearest to the surface, which helped to reduce the time to reach intraparticle diffusion and all the particles were treated in the same way, ensuring high uniformity.

**Figure 2.** Pseudo-first- and pseudo-second-order kinetics of AnMBR permeate with Purolite SSTC60.

However, despite the high adsorption rate, the maximum adsorption capacity was reduced by 28% less than with N-Z so that an even greater difference was expected working with Na-Z since SAC has a greater affinity for divalent cations, such as Ca^{2+} or Mg^{2+} , as can be seen in Figure 3, in which these cations are reduced to practically zero. This makes the ammonium to compete for exchange sites and reduces ammonium adsorption. Two columns in a series are thus required when water with a high divalent cation concentration is treated: one to remove the Ca^{2+} and Mg^{2+} and another to retain the NH_4 . Figure 3 shows how the Na^+ present in the resin is released in the exchange process with the rest of the cations.

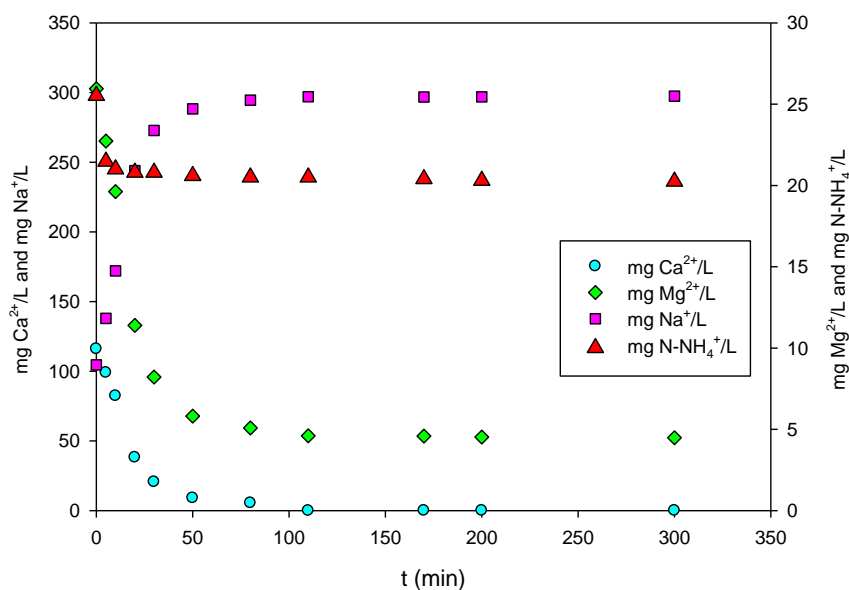


Figure 3. Evolution of the concentration of the main cations during the development of kinetics with Puroilite SSTC60.

3.2. Effect of Zeolite Activation and Particle Size

A batch experiment with three different particle sizes (500–1000 μm, 600–1800 μm, and 1000–2500 μm) and distilled water fortified with NH₄Cl were first carried out to find the one with the highest ammonium adsorption. The results of this preliminary test showed that the smaller the particle size, the better the performance (Table 3). This has been found by many other authors, as, due to the reduced particle size, the specific surface area of the zeolite increases so that the ammonium and other cations are more easily exchanged for the cations present in the aqueous solution [22,23]. For this reason, a zeolite with a particle size of 500–1000 μm was used in the remaining tests.

Table 3. Adsorption capacity of natural zeolite when C₀ = 30 mg N-NH₄/L.

Particle Size (μm)	q _e (mg N-NH ₄ /g)
500–1000	2.86
600–1800	2.69
1000–2500	2.57

Activating zeolite in its Na- form is known to improve its performance as it allows the exchange sites to be occupied by sodium ions [24,25]. Since the alkaline metal cation content with a small hydrated radius increases (large ionic radius and low valence), the ammonium adsorption capacity is also raised [14]. In some studies zeolites were treated with thermal calcination combined in the chemical attack with NaCl [26] while others preferred to use only NaOH as activation reagent [27]. In the present study zeolites were activated in contact with 1M NaOH for one hour and then neutralized the pH with carbonated water. The results show that on average the performance increased by 20% after applying this activation process (Figure 4). A similar improvement of 27% was found by [28] when they activated a natural clinoptilolite with Na. Furthermore, the procedure employed in this research based on adjusting the pH after activation by means of CO₂ stripping allows the decrease of the amount of washing water in 90% compared adjusting the pH of the zeolite by successive washings.

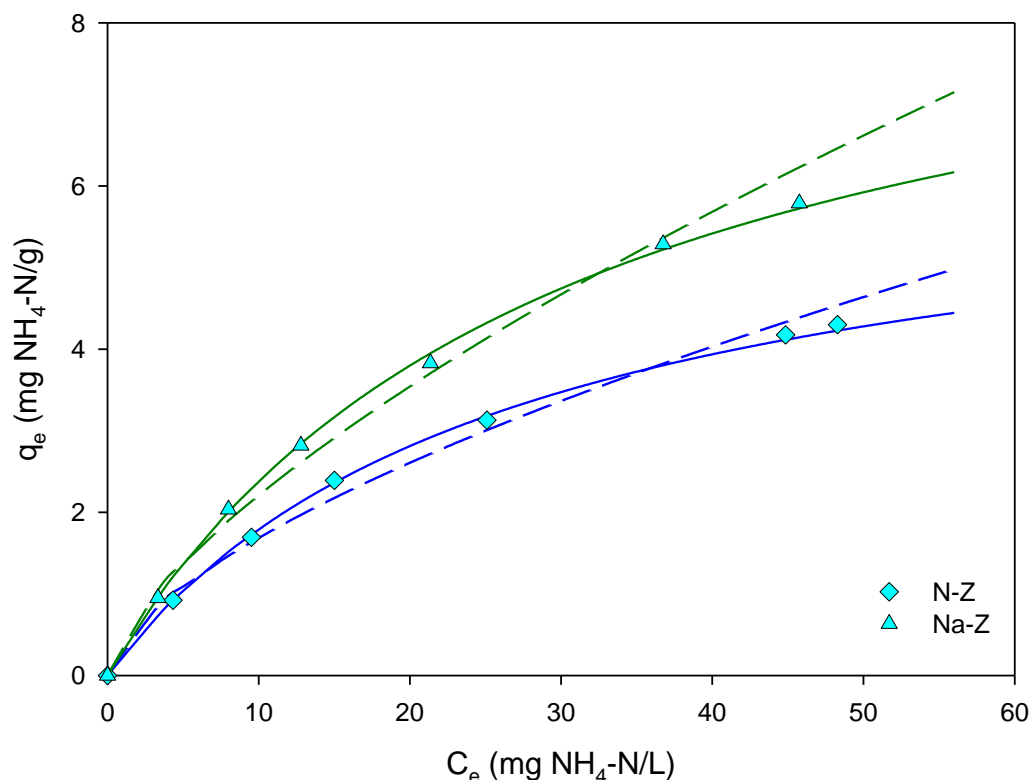


Figure 4. Comparison of the isotherms carried out with the natural zeolite (N-Z) and the zeolite activated by NaOH (Na-Z) together with the adjustment of both experimental data by the Langmuir (continuous line) and Freundlich (dashed line) models.

Pretreated NaOH enhances ammonium adsorption not only due to reducing the Ca/Na ratio, as some authors have found [24], but because this treatment also causes changes in the zeolite structure. The right NaOH concentration can generate a greater number of mesopores and micropores, which improves ammonium ion diffusion in the zeolite particles [29]. However, a concentration of 3 M NaOH or higher causes the opposite effect, destroying its mesoporous structure and thereby reducing its adsorption capacity [28].

In the present study we made the rest of the isotherms with the activated zeolite in the Na form since it better represents the operating conditions when working with this adsorbent material in cation exchange columns to treat AnMBR permeate. Since the exchange columns combine loading cycles in which the ammonia is retained, followed by a regeneration cycle that releases and concentrates it (Qin et al. [30] reviewed different studies and observed an ammonium concentration factor between 8–20 times). For the regeneration phase, reagents containing sodium (NaCl or NaOH, for example) are normally used so that after regeneration, the zeolite is in the Na form. For this reason and since activation by Na has a significant effect on the adsorption capacity, it was decided to make the rest of the isotherms using activated zeolites.

Figure 4 shows the fitting of the Na-Z experimental data with the Langmuir and Freundlich isothermal models. It should be noted that unlike other works that studied maximum adsorption capacity of the zeolite working with high ammonium concentrations [12,24], in this work, the ammonium concentration, obtained from AnMBR permeate, was significantly low.

As can be seen in Table 4, the Langmuir model fits better with the experimental data, as has been found by many other authors [12,13,18] who emphasise the fact that both models fit correctly when working with low ammonium values, but for higher concentrations, only the Langmuir model allows a good fit. This is because the Freundlich model does not consider an intrinsic limit to the zeolite capacity while the Langmuir model considers that all the adsorbent material has a limited number of exchange points. However, the

Langmuir model also fails to consider the true nature of ion exchange in which one species displaces the other, altering the concentration of both [31].

Table 4. Analysis of the adjustment parameters for the isotherm models for the N-Z and Na-Z.

	Langmuir		Freundlich			
	K_L	q_{max}	RMSE	K_f	$1/n$	RMSE
Distilled water N-Z	0.037	6.56	0.058	0.396	0.629	0.195
Distilled water Na-Z	0.033	9.44	0.078	0.459	0.682	0.268

Since the Freundlich fit can also be applied at low concentrations, conclusions can be drawn from the constant $1/n$. This constant gives an approximation of how favourable the adsorption will be. The lower the values of $1/n$, the more heterogeneous the adsorption [32]. N-Z and Na-Z have a value of $1/n$ of 0.629 and 0.682, respectively, so that being a value less than 2.0, it can be said that this material does not present difficulties to the ammonium adsorption process.

3.3. Competing Ions

The isotherms obtained from fortified distilled water were compared with the data obtained from tap water fortified only with ammonium and with ammonium and phosphate. PO_4 was added in the same concentration as that found in the AnMBR permeate to determine its possible effect on adsorption.

As can be seen in Table 5, ammonium removal capacity was reduced by 22% in the presence of cations, such as Ca^{2+} , K^+ , Mg^{2+} , or Na^+ , in the tap water. The effect of the competition of the cations for the active centres of exchange has been reported by other authors. Thornton et al. [13] found a similar reduction in the zeolite effectiveness, with a 30% loss of ammonium adsorption in the presence of the cations, mostly Ca^{2+} . Wang et al. [10] found less interference between 10–20% while Mazloomi and Jalali [33] considered that the influence can rise by up to 50%. Although there are differences in the reduction value, all the results indicate that the cations compete strongly with the ammonium in adsorption, thus reducing their exchange capacity.

Table 5. Adsorption capacity (q_e) in the different isotherm tests carried out when $C_e = 28.8$ mg NH_4 -N/L.

	q_e (mg/g)
Distilled water N-Z	3.42
Distilled water Na-Z	4.66
Tap water Na-Z	3.63
Tap water + PO_4 Na-Z	3.66
Tap water + methanol Na-Z	4.53
Tap water + glucose Na-Z	4.59
AnMBR permeate	4.06

Due to the affinity of zeolite for different cations, it was found that it is not affected equally by all of them. As explained above, the natural zeolite studied has a greater affinity for monovalent than bivalent cations. However, considering the concentration in which the cations are present in the working water (Table 1), it can be said that Na^+ and Ca^{2+} are the main cations in competition with NH_4^+ . The individual effect of each cation has been studied by other authors, who concluded that different zeolites respond differently to the competition for ammonium according to the preference of the adsorbent material. While Huang et al. [34] and Weatherley and Miladinovic [35] suggest that Ca^{2+} is the main competitor, others such as Lei et al. [14] or Sprynskyy et al. [36] pointed to Na^+ as the cation responsible for the reduced ammonium removal capacity. However, unlike these cited works, our tests determined the effect of the mix of cations in the AnMBR permeate in order to understand the adsorption capacity values obtained by our real working water.

The influence of phosphate was analysed in regard to the possible interference of the anions in the real working water. Figure 5 shows how the PO_4 concentrations in the AnMBR permeate have no impact on the ammonium removal capacity. This is because of the low concentrations of PO_4 (3.3 mg- PO_4 -P/L), which is lower than the values required to produce an interaction. Mazloomi and Jalali [33] found that at higher concentrations, PO_4 causes ammonium adsorption drop up to 65%.

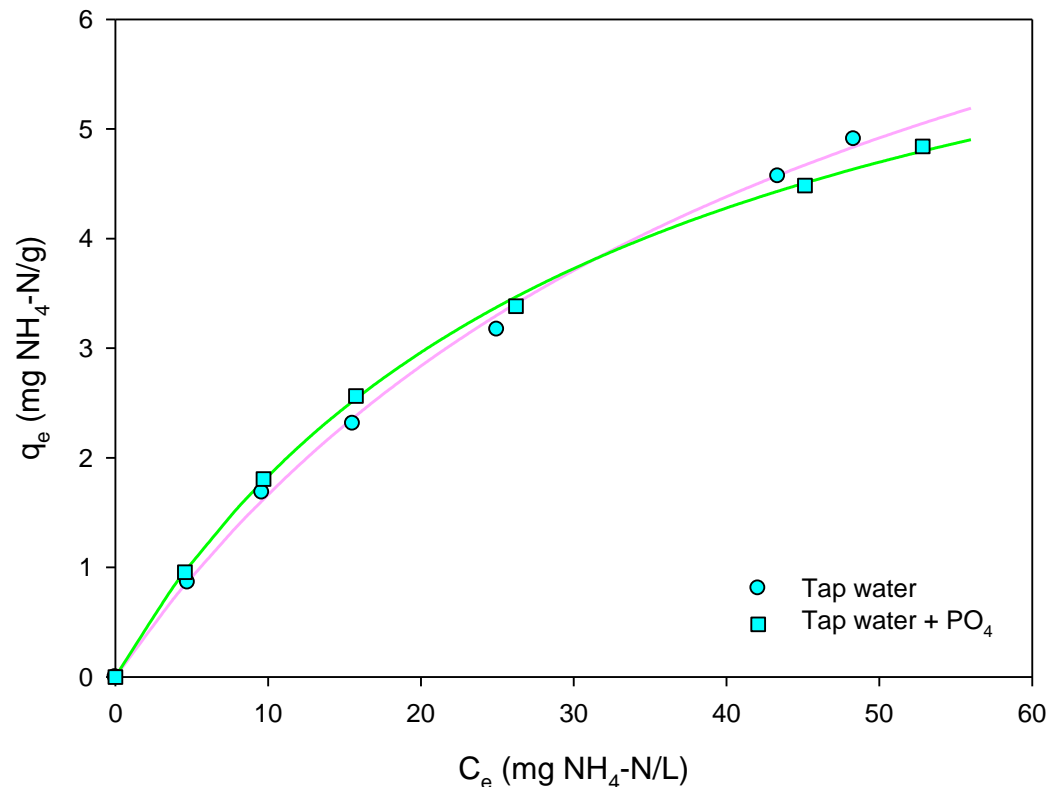


Figure 5. Comparison of isotherms performed with tap water and tap water fortified with PO_4 . Only the Langmuir model fit shown.

Other authors, such as Huang et al. [22] and Guaya et al. [37], have pointed out that the affinity of zeolites for PO_4 is lower than the one observed for other anions in the wastewater (CO_3 having the highest affinity, followed by Cl^- and SO_4). Given the low concentration of PO_4 in the permeate and its low affinity, this anion, therefore, does not affect the adsorption capacity.

In relation to this low affinity, phosphate adsorption was not observed after 4 h of contact. Some studies [17,37,38] pointed out the need to modify the N-Z in order to remove PO_4 . The incorporation of hydrated metal oxides such as Fe^{2+} , Al^{3+} , or Mn^{2+} is often used to retain up to 90% of the influent phosphate. With no pretreatment of this type in the present study, the reduction of PO_4 when working with the AnMBR permeate was not expected.

3.4. Effect of Organic Matter

Figure 6 shows how the presence of organic compounds significantly improved the adsorption capacity of the zeolite studied (22%). However, no differences were found between the two organic substrates, indicating that both have the same effect on the matrix. Other authors, such as Jorgensen and Weatherley [39], have detected similar behaviour in ammonium removal capacity in the presence of whey protein and lipase and attributed the reduction in the surface tension of the water to the presence of organic matter. Reducing the water surface tension improves ammonium diffusion in the zeolite particles and allows the fluid to access previously inaccessible pores. Lei et al. [14] confirmed this hypothesis by

analysing the water surface tension variation as the organic matter in the working matrix increases and its effect on ammonium adsorption capacity. Their results indicate that for humic acid values of 10 mg/L or higher the changes in surface tension are significant and that the maximum ammonium adsorption capacity is improved.

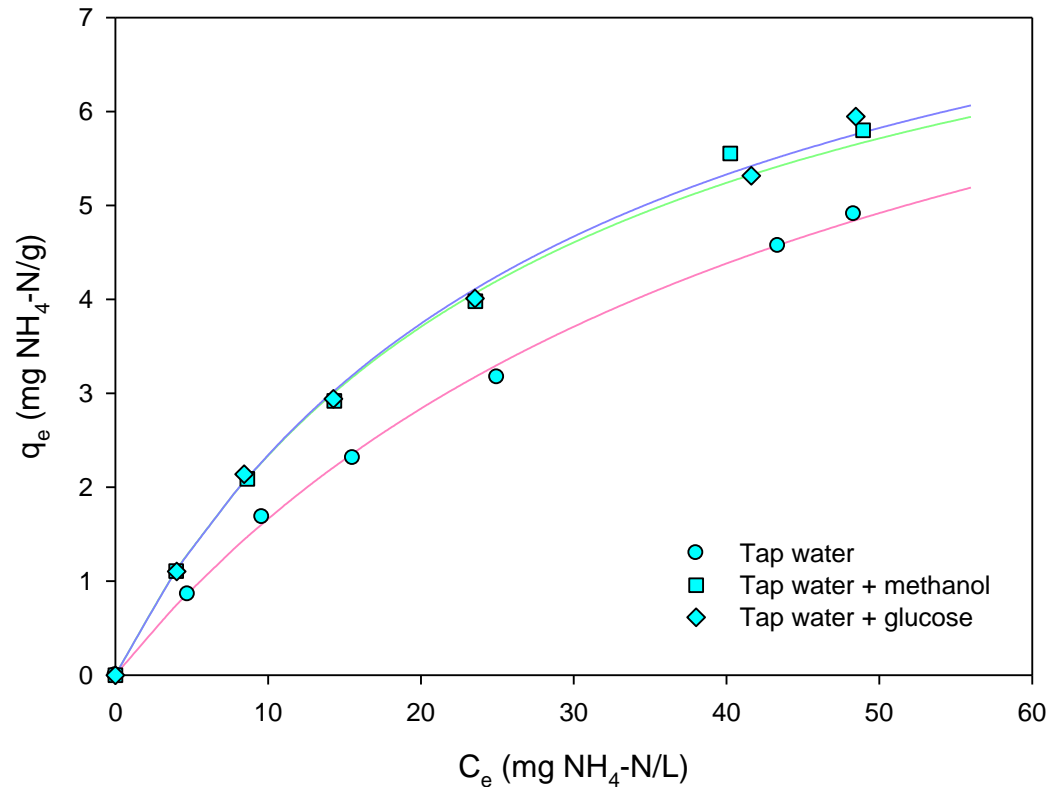


Figure 6. Comparison of isotherms performed with tap water and fortified tap water enriched with different organic substrates. Only Langmuir model fit shown.

Other authors, such as Yin and Kong [15] or Guaya et al. [37], found that if the organic matter is in high concentrations the opposite effect is achieved, thus reducing the amount of ammonium retained. This may be due to the fact that high concentrations of hydrogen ions can compete with the ammonium for the sites available for exchange. H. Huang et al. [34] point out that at high organic matter concentrations, pH can be affected and become acidic, making it necessary to add NaOH to buffer the matrix. This contribution of Na⁺ to the system reduces the ammonium adsorption capacity since it competes directly with the ammonium.

However, since AnMBR retains all the suspended organic matter and part of the soluble organic matter, no high concentration of organic matter in the permeate is expected, so the adverse effect of organic substrates is not considered.

3.5. pH Effect

The zeolite adsorption capacity has been studied working in a pH range of 4 to 9 and using HCl and NaOH to modify the pH. The results indicate that the zeolite obtains its highest adsorption for pH values between 6–7 while outside this range the capacity is reduced (Figure 7), although it is higher when the pH tends towards basic values.

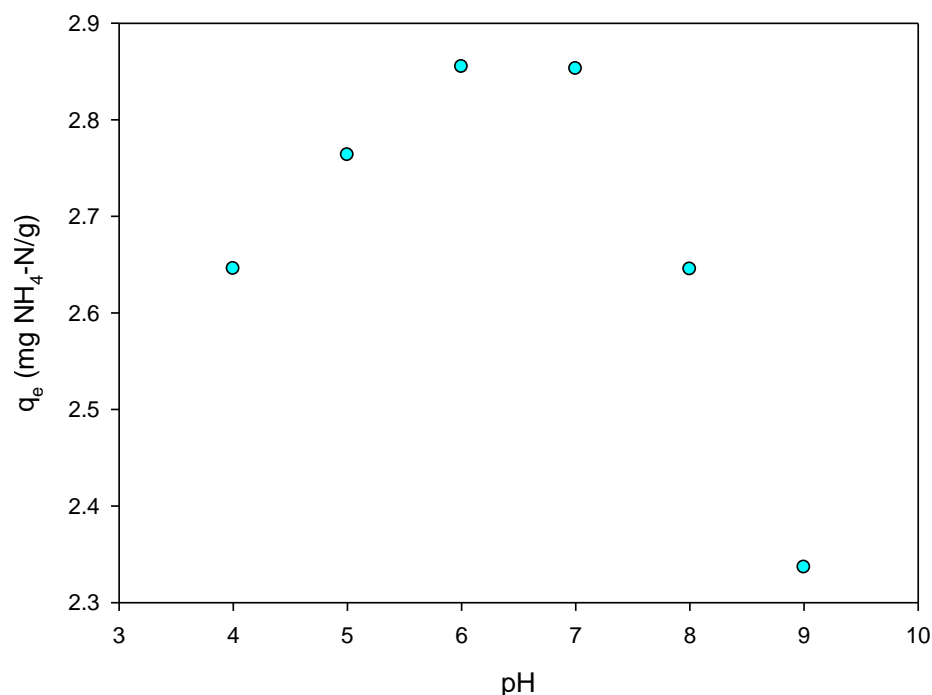


Figure 7. Behavior of the q_e as a function of pH.

The differences in efficiency reduction are due to different mechanisms. When pH is less than 7, the hydrogen ion concentration increases. These ions compete directly with the ammonium for the exchange sites of the zeolites. Therefore, the reduction obtained is due to the competition of these two cations [19].

On the other hand, when pH becomes basic, the dissociation equilibrium of ammonium in water tends towards the species forming ammonia (NH_3). As pH rises, the dominance of NH_3 versus NH_4^+ also rises. This is why adsorption is drastically reduced with basic pH since in this case, it is not an effect due to the competition for the exchange sites but, rather, the NH_4^+ is transformed into NH_3 , a species that is not interchangeable at the active points of the zeolite because it has no surface charge [16].

Based on the pH data recorded in the permeate of the AnMBR pilot plant (Table 1 shows that the average pH is 7.2), pH is not expected to generate interference when working with the zeolites to retain the ammonium

3.6. Effect of AnMBR Permeate

The data indicate that the adsorption with AnMBR permeate is higher than when working only with tap water (Table 5) since tap water has a higher Na^+ concentration than the AnMBR permeate plus the presence of organic components. As mentioned above, Na^+ and Ca^{2+} were responsible for the reduced ammonium adsorption associated with water hardness. On the other hand, the data fit better with the test with tap water enriched with organic matter, confirming the idea that the organic substrate improves the ammonium removal capacity of the zeolite. Neither PO_4 nor pH were found to have a clear influence on the exchange capacity when working with AnMBR permeate.

Since the isotherms have been made with ammonium concentrations similar to those expected in the AnMBR permeate, the same conclusions can be drawn regarding the degree of fit with the Langmuir and Freundlich models. The Langmuir model fits better with the experimental data (Figure 8), although Freundlich also offers a good fit, obtaining a coefficient of $1/n = 0.43$. This value suggests that the zeolites provide good adsorption with this working matrix [32].

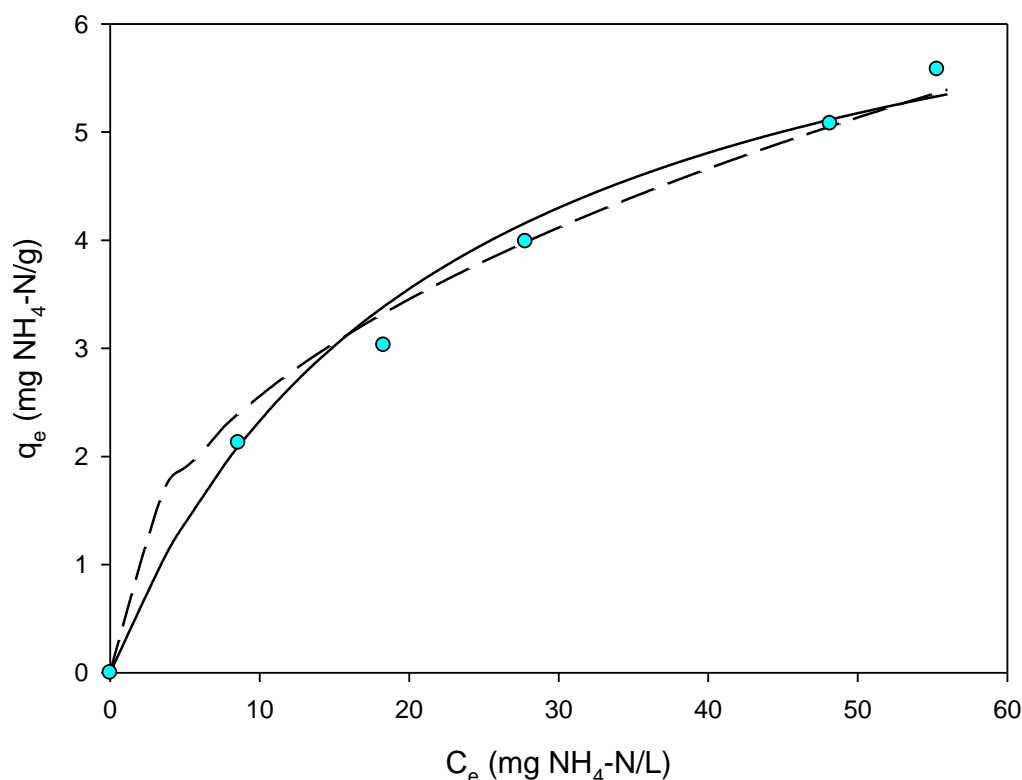


Figure 8. Experimental and theoretical equilibrium isotherms for ammonium removal by Na-Z with AnMBR permeate. Langmuir (continuous line) and Freundlich (dashed line) models.

The value of the maximum ammonium adsorption capacity (q_{max}) obtained by adjusting the Langmuir isotherm shows that the treatment of the AnMBR permeate with zeolites in an exchange column is feasible. A q_{max} value of 7.44 mg/g has been obtained, which is in the ranges achieved by other authors in similar conditions (Table 6). For example, Millar et al. [24] obtained values of 6.72 and 10.4 mg N-NH₄/g working with two natural zeolites and synthetic water, showing again the effect of activate zeolite previously. In these adsorption ranges, Mazloomi et al. [33] obtained between 8.51 and 10.39 mg N-NH₄/g depending on the absence or presence of cations in the working water. The capacity loss by these components in real water is similar to the one reported in the present study. Similar adsorption values were obtained by Alshameri et al. [16] also working with a clinoptilolite-Na. It is important to know the ammonium concentration at which the adsorption capacity value has been obtained, since this parameter has a great influence on the maximum adsorption capacity. For example, while Al-Sheikh et al. [11] obtained a 1.2 mg N-NH₄/g capacity working at 22.7 mg N-NH₄/L, Guaya et al. [38] and Jmayai et al. [12] obtained 23 and 51.8 mg N-NH₄/g, respectively, but working at a concentration of 5000 mg N-NH₄/L. It is also important to consider the adsorbent material used when comparing the results, since, as explained previously, the SACs have a greater exchange capacity (Sica et al. [40] obtained 28.23 employing SAC called Purolite C150H). Although this high adsorption can be seriously compromised in the presence of divalent cations, such as Ca²⁺ or Mg²⁺. The adsorption capacity value achieved for ammonium (q_{max} value of 7.44 mg/g) ensures that if the cation exchange column is designed appropriately, the effluent obtained will meet discharge requirements in sensitive areas and the nitrogen present in the influent can be recovered. A subsequent column study will be necessary to determine the appropriate operating conditions to ensure a quality effluent and to extend the useful life of the zeolite.

Table 6. Comparison of adsorption capacity (q_e) by different adsorbents and ammonium concentration.

Adsorbent	Influent	Maximum Ammonium Concentration (mg NH ₄ -N/L)	Adsorption Capacity (mg NH ₄ -N/g)	Reference
Clinoptilolite-Na	Synthetic	70	9.44	This study
Clinoptilolite-Na	AnMBR permeate	70	7.44	This study
Bentonite	Synthetic	311	6.72	[24]
Bentonite-Na	Synthetic	311	10.40	[24]
Purolite C150H	Synthetic	150	28.23	[40]
Clinoptilolite	Synthetic	5000	51.8	[12]
Clinoptilolite-Na	Real wastewater	22.7	1.2	[11]
Clinoptilolite-Na	Synthetic	250	11.18	[16]
Clinoptilolite-Mn	Synthetic	5000	23	[38]
Clinoptilolite	Synthetic	40	10.39	[33]
Clinoptilolite	Synthetic + Cations	40	8.51	[33]

4. Conclusions

In the present work, the adsorbent material to recover nitrogen from the AnMBR permeate has been selected and characterized. N-Z showed better retention ammonium capacity than SAC due to the presence of divalent cations in the AnMBR permeate. The characterization of the zeolite by means of isotherms allowed us to know the effect of different parameters over the ammonium adsorption capacity (zeolite activation, particle size, and water characteristics, such as pH, ions and organic matter). The activation process with NaOH and subsequent neutralization with water and CO₂ has improved the performance by 20% and reduced water consumption in this stage up to 90%.

As expected, the presence of cations such as Ca²⁺ and Mg²⁺ reduced a 22% the ammonium retention working with N-Z, due to the competition for the active sites. While the organic matter present in the AnMBR improved N-Z performance, increasing it up to 22%. The Langmuir model better represents the behavior of the isotherms. Although when working with low ammonium concentrations, the Freundlich model also shows a good fit, and a heterogeneous adsorption can be concluded from the constant $1/n = 0.682$.

This study confirmed the feasibility of clinoptilolite for nitrogen recovery from the permeate obtained in the AnMBR process (a q_{max} adsorption value of 7.44 mg NH₄-N/g has been obtained). On the other hand, it is necessary to continue the study of this material in a cation exchange column to define the operating parameters and the regeneration performance.

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