

Article

Potential Application of Chilean Natural Zeolite as a Support Medium in Treatment Wetlands for Removing Ammonium and Phosphate from Wastewater

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Abstract: This study aims to evaluate the sorption characteristics of $\text{NH}_4^+\text{-N}$ and $\text{PO}_4^{3-}\text{-P}$ onto the surface of natural zeolites coming from Chile and their potential application in the subsurface-flow treatment wetlands for wastewater treatment in rural areas. For this purpose, adsorption experiments onto the zeolite were developed in batch assays. The effects of the adsorbent quantity (20 g and 50 g) and particle size (0.2–1.0 mm; 1.5–3.0 mm, and 5.0–8.0 mm) were evaluated in terms of adsorption capacity at different $\text{NH}_4^+\text{-N}$ and $\text{PO}_4^{3-}\text{-P}$ concentrations. Then, the obtained laboratory results were adjusted to theoretical models: Saturation-growth-rate and Langmuir. The saturation adsorption of $\text{NH}_4^+\text{-N}$ on the zeolite increases at the same time that the initial concentration increases for the same zeolite quantity; however, the saturation values were similar between the different zeolite sizes tested. For $\text{PO}_4^{3-}\text{-P}$, the adsorption did not have a direct relationship with the initial concentration nor zeolite quantity and better results were only achieved for zeolite sizes of 1.5–3.0 mm. Regarding the Langmuir model, sizes of 1.5–3.0 mm had the best adsorption characteristics, with the maximum adsorption capacity of up to 1.58 mg/g for $\text{NH}_4^+\text{-N}$ and up to 0.08 mg/g for $\text{PO}_4^{3-}\text{-P}$. Therefore, a new material—a natural zeolite from the Maule Region of Chile—is described as a potential support medium for treatment wetlands.

Keywords: ammonium; Chile; phosphate; natural zeolite; treatment wetlands

1. Introduction

Subsurface-flow treatment wetlands (SSF-TWs) are an alternative to traditional activated sludge systems for the treatment of wastewater in rural areas [1,2]. When SSF-TWs are used in wastewater

treatment plants (WWTP), the removal efficiency of nitrogen and phosphorus is below 60% and, usually, it is below 40% [3–5]. However, in SSF-TWs, the removal process can be intensified by different operational strategies and innovative designs, thus improving removal efficiencies to reach levels of 50–90% [6–8]. One of these operational strategies is the use of media to enhance the adsorption process, and natural zeolites are one of the potential removal media studied for use in TWs [9,10].

Natural zeolites are promising as a support medium in SSF-TWs because they are abundant, relatively inexpensive (0.6–1.6 USD/kg), have appropriate hydraulic characteristics, and have regenerative capacities [9–11]. Natural zeolites are minerals with a porous structure that have valuable physicochemical properties, such as cation exchange capacity (sodium, potassium, or calcium), molecular sieving, catalysis, and sorption [12–14]. The ion exchange that results from the negative charge on the zeolite's surface and the sorption capacities are important for NH_4^+ -N removal [15], while precipitation with divalent and trivalent metal cations and the sorption onto natural zeolite are important for PO_4^{3-} -P removal [16,17]. These two inorganic compounds are the main components of the total nitrogen and the total phosphorus found in domestic wastewaters (NH_4^+ -N, 60–65% of the total nitrogen; PO_4^{3-} -P, above 60% of the total phosphorus). Consequently, their removal is a key factor for nutrient removal from domestic wastewater [18–20].

When conventional support media, such as gravel or sand, are used in SSF-TWs, the adsorption contributes to at least 30% of the N removal by sequestering NH_4^+ -N [15,21]. However, when natural zeolites are used in SSF-TWs, the NH_4^+ -N removal efficiency can be increased up to 70% [15,22]. In the case of phosphorus, SSF-TWs with traditional support medias show removal efficiencies below 40% and tend to decrease over time as the adsorption capacity is used up [5,21–24]. However, when natural zeolites are used as media in SSF-TWs or as external filters, the removal efficiency can be increased up to 70% [25,26].

Different studies have shown that Chilean natural zeolites can be used to remove NH_4^+ -N and PO_4^{3-} -P from different wastewater types [10,15,26–29]. For SSF-TWs, Vera et al. [26] and Andrés et al. [10] showed characteristics for PO_4^{3-} -P removal and their application in mesocosm SSF-TWs. Araya et al. [15] showed the pathways of NH_4^+ -N removal when natural zeolites, with induced aeration for nitrification, were used as strategies to increase its removal from wastewater. However, a specific study for the determination of the sorption characteristics of NH_4^+ -N and PO_4^{3-} -P, using Chilean zeolites to assess their actual capacity for use with SSF-TWs to treat domestic wastewater from rural areas has not yet been developed.

Determining the sorption characteristics is the first step. The Langmuir and Freundlich adsorption kinetic models have been used to determine the adsorption capacities for natural zeolites and other materials that have a sorption potential [9,30–32]. For instance, in the case of phosphorus, maximum adsorption capacities between 0.3 and 6.8 mg P/g have been determined for natural zeolites [9,33,34]. These values are useful for estimating the operational parameters of SSF-TWs when natural zeolite is employed as a support medium and SSF-TWs are used in continuous operation.

Taking the above into account, the aim of this work was to evaluate the sorption characteristics of NH_4^+ -N and PO_4^{3-} -P onto the surface of natural zeolites coming from the Maule Region in Chile and their potential application in subsurface-flow treatment wetlands for wastewater treatment in rural areas.

2. Materials and Methods

2.1. Zeolite

Natural zeolite was used as the adsorbent material for ammonium and phosphate. A local company, “Zeolitas del Maule,” supplied the material. The material was extracted from two deposits located at Quinamavida, Colbún, in the Region of Maule (Southern Chile). The mineralogical and chemical composition was taken from the product datasheet provided by the local supplier (Table 1). Three main minerals compose the zeolite: clinoptilolite, mordenite, and heulandite.

Table 1. Chemical composition of the natural zeolite used as the adsorbent material.

Molecule	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	Na ₂ O	TiO	P ₂ O ₅	Losses by Combustion
Composition (%)	64.2	11.7	3.4	2.5	1.6	0.7	0.8	0.5	0.1	14.5

Regarding physical characteristics, natural zeolites have a Brunauer–Emmett–Teller (BET) surface area of 446 to 480 m²/g and a cation exchange capacity (CEC) of 86.82 to 112.88 cmol/kg.

2.2. Batch Assays for the Study of Adsorption Characteristics

Adsorption experiments onto the zeolite were developed in batch assays [10,35]. The effects of adsorbent quantity (zeolite quantity) and particle size were evaluated in terms of adsorption capacity [36,37]. Two different adsorbent quantities were studied—20 g and 50 g—in agreement with Andrés et al. [10]. Three zeolite sizes were tested: a) 0.2–1.0 mm, b) 1.5–3.0 mm, and c) 5.0–8.0 mm. The batch assays are summarized in Table 2. These experiments were carried out in random order. The selection of zeolite size was based on commercial availability and on the fact that natural zeolite sizes, ranging from 0.5 to 10 mm, have previously been employed in some SSF-TWs for wastewater treatment [38–40].

Table 2. Experimental design used in NH₄⁺-N and PO₄³⁻-P assays for the determination of adsorption characteristics.

Batch Assay	Zeolite Amount (g)	Particle Size (mm)	NH ₄ ⁺ -N Initial Concentration (mg/L)	PO ₄ ³⁻ -P Initial Concentration (mg/L)
1	20	5.0–8.0	85, 65, 45, 25	15, 10, 5, 1
2	50	5.0–8.0	85, 65, 45, 25	15, 10, 5, 1
3	20	1.5–3.0	85, 65, 45, 25	15, 10, 5, 1
4	50	1.5–3.0	85, 65, 45, 25	15, 10, 5, 1
5	20	0.2–1.0	85, 65, 45, 25	15, 10, 5, 1
6	50	0.2–1.0	85, 65, 45, 25	15, 10, 5, 1

In trials, the initial NH₄⁺-N concentrations were evaluated with solutions containing 25, 45, 65, and 85 mg/L (Table 1). In the case of PO₄³⁻-P, the initial concentrations were evaluated with solutions containing 1, 5, 10, and 15 mg/L (Table 1). These initial concentrations are typically found in domestic wastewaters, including those produced in rural areas in Chile [15,18,26]. Each aliquot was prepared in an Erlenmeyer acid-washed flask that could contain 200 ml of distilled water, with an NH₄⁺-N concentration prepared from an NH₄Cl and PO₄³⁻-P concentration using KH₂PO₄ stock solutions to reach the desired concentrations, and with the corresponding zeolite weight (20g or 50g). All the samples were tested in duplicates and shaken in the Orbital Laboratory Stirrer at 20 ± 0.1 °C and 100 rpm. Independent trials for NH₄⁺ and PO₄³⁻ were conducted to evaluate adsorption behavior separately. The trials were developed separately since, according to Karapinar [41] synergic effects (positive or negative) do not occur with the simultaneous removal of ammonium and phosphorus by natural zeolites. Two controls were used. At the beginning, microbiological activity was checked with a control using a sterilized zeolite and concentrations of 85 mg/L and 15 mg/L for NH₄⁺-N and PO₄³⁻-P, respectively. This check was developed to control the microbial activity in batch assays because only the physic-chemical effect was desired for the study. The zeolite was sterilized in an autoclave (20 min at 105 °C) [42–44]. Afterwards, the desorption effect was analyzed with a blank, using the zeolite, a 0 mg/L concentration of NH₄⁺-N, and a 0 mg/L concentration of PO₄³⁻-P. The NH₄⁺-N concentration in the liquid was monitored every 30 min until saturation or for a maximum 8-h period. The PO₄³⁻-P concentration in the liquid was monitored at different times during a maximum 216-h period (0, 4, 8, 24, 28, 32, 48, 52, 56, 72, 76, 80, 96, 100, 104, 120, 168, and 216 h).

2.3. Analytical Methods

PO_4^{3-} -P and NH_4^+ -N were measured photometrically using multiparameter photometer HANNA HI-83,399 reagent test kits: a) PO_4^{3-} -P, HI93713 and HI93717; b) NH_4^+ -N, HI93715 and HI93733 (see Table 3) [45,46]. These determinations are modifications of standard procedures from APHA-AWWA-WEF (2017) [47]. The pH and temperature were measured using portable HI 98,194 equipment.

Table 3. Technical specifications for HANNA HI-83,399 reagent test kits.

Parameter	Range (mg/L)	Resolution (mg/L)	Accuracy of Reading at 25 °C (mg/L)	Light-Emitting Diode (LED)* (nm)	Method
Phosphate low range (HI93713)	0.00 to 2.50	0.01	$\pm 0.04 \pm 4\%$	610	Ascorbic acid
Phosphate high range (HI93717)	0.00 to 30.00	0.10	$\pm 1 \pm 4\%$	525	Amino acid
Ammonia medium range (HI93715)	0.00 to 10.00	0.01	$\pm 0.05 \pm 5\%$	420	Nessler
Ammonia high range (HI93733)	0.00 to 100.00	0.10	$\pm 0.5 \pm 5\%$	420	Nessler

*with narrow band interference filter.

2.4. Adsorption Modelling

The removal of PO_4^{3-} -P and NH_4^+ -N by zeolite adsorption can be considered to be a saturation-growth-rate equation as a function of adsorption time, like the one proposed by the Langmuir adsorption kinetic model [10,48]. The saturation-growth-rate equation is a nonlinear model that was fitted with the experimental data in order to determine the adsorption rate for only one batch assay. This equation is as follows:

$$m = \frac{m_{\max} \times t}{t_{1/2} + t} \quad (1)$$

where t is the time (h), m is the amount adsorbed on a defined amount of adsorbent (mg/g), $m_{\max}$ is the maximum amount adsorbed on a defined amount of adsorbent (mg/g), and $t_{1/2}$ is the time for m to be half $m_{\max}$.

Furthermore, the Langmuir adsorption kinetic model was also used to fit the experimental data from the batch test because, unlike the saturation-growth-rate model, the Langmuir model can cluster different batch assays. The Langmuir model has previously been used to evaluate the adsorption process onto different materials [49–51]:

$$q = Q \times \left(\frac{b \times C_e}{1 + b \times C_e} \right) \quad (2)$$

where q is the mass of adsorbate per mass unit of adsorbent at equilibrium (mg/g), C_e is the equilibrium adsorbate concentration (mg/L), Q is the maximum mass adsorbed at saturation conditions per mass unit of adsorbent (mg/g) (maximum adsorption capacity), and b is the empirical constant with units of inverse concentration (L/mg) [52]. Furthermore, b can be considered to be an energy adsorption indicator onto the adsorbent. In the Langmuir model, Q and b can be estimated by regression.

2.5. Statistical Analysis

Statistical analyses were used to evaluate measured and calculated parameters for natural zeolite as the adsorbent material. First, the mean and standard deviation of triplicate results were determined. Second, the degree of intensity or effectiveness that independent variables have in explaining dependent variables in the multiple applied regressions, i.e., the saturation-growth-rate equation and Langmuir model, was determined by R^2 and adjusted R^2 (R^2_{adj}):

$$R_{\text{adj}}^2 = 1 - \left[\frac{n-1}{n-k-1} \right] \times (1 - R^2) \quad (3)$$

where n is the experiment number, k is the independent variable number and R^2 is the coefficient of determination. Third, the data were subjected to a normality test (i.e., a Shapiro–Wilk Test) to determine the statistical tests for comparison. Fourth, to compare (1) the zeolite’s adsorption capacity and the initial concentration, (2) the zeolite’s adsorption capacity and the zeolite sizes, and (3) the zeolite’s adsorption capacity and the zeolite weight, the following tests were performed, (a) data with normal distribution, one-way ANOVA test and (b) data without normal distribution, the Kruskal–Wallis test. All statistical tests were performed using InfoStat[®] with a significance level $\alpha = 0.05$.

3. Results and Discussions

3.1. Batch Assays for Adsorption Characterization

Figure 1 shows the results of NH_4^+ -N adsorption onto Chilean natural zeolite for the batch experiments. The saturation adsorption of NH_4^+ -N to the zeolite varied between 0.05 and 0.7 mg/g. In addition, the saturation adsorption of NH_4^+ -N increased at the same time that the initial concentration in the solution increased for the same zeolite weight but the saturation values were similar among the different zeolite sizes (Figure 1). This result shows the positive relationship between two variables ($p < 0.05$)—the zeolite’s adsorption capacity and the initial concentration—but it does not show a relationship between the tested zeolite sizes ($p > 0.05$). This characteristic is important for the use of Chilean natural zeolite as a support medium in treatment wetlands and the possibility of using its various sizes was tested in this work (0.2–1.0 mm, 1.5–3.0 mm, and 5.0–8.0 mm). In addition, when the zeolite quantity increased from 20 g to 50 g (2.5 times), the adsorbed NH_4^+ -N onto zeolite increased between 1.5 and 3.0 times at the same initial concentration and zeolite size.

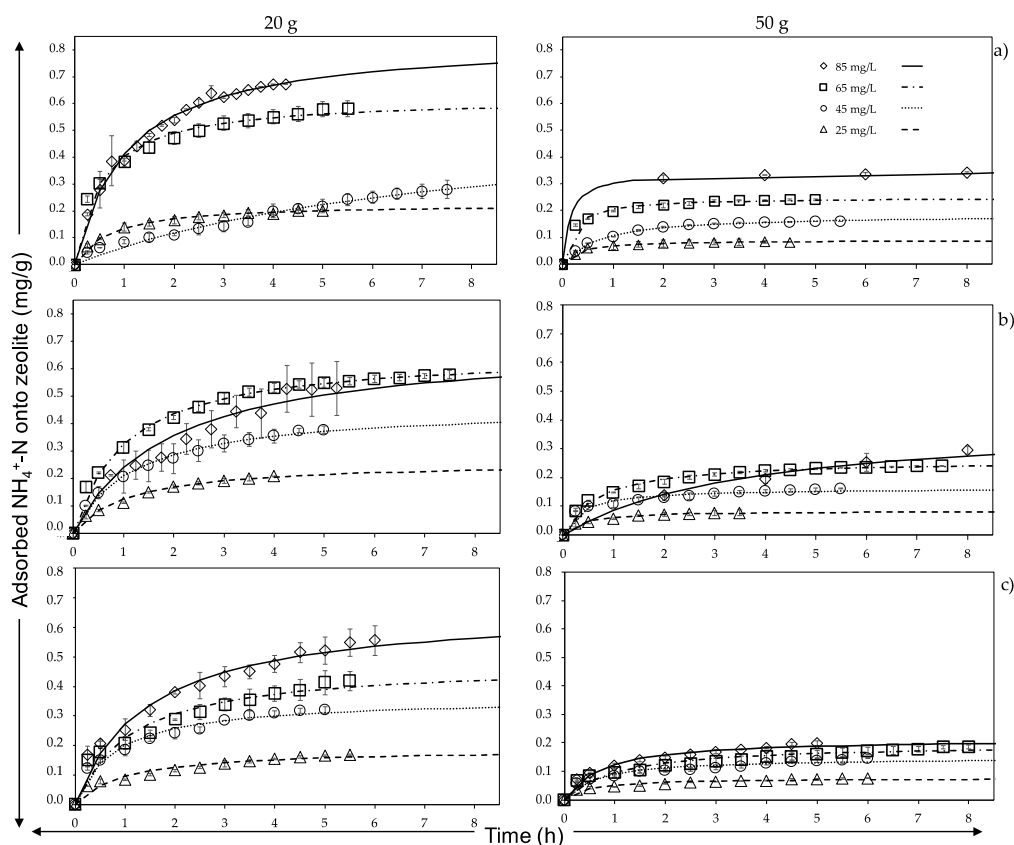


Figure 1. Adsorbed ammonium (mg/g) onto zeolite vs. time in batch assays for the determination of adsorption characteristics. Particle size: (a) 5.0–8.0 mm; (b) 1.5–3.0 mm; and (c) 0.2–1.0 mm.

Figure 2 shows the results of $\text{PO}_4^{3-}\text{-P}$ adsorption onto the tested zeolite. The saturation adsorption of $\text{PO}_4^{3-}\text{-P}$ varied from 0.001 to 0.04 mg/g. In comparison to the adsorption of $\text{NH}_4^+\text{-N}$, the $\text{PO}_4^{3-}\text{-P}$ did not show a direct relationship with the initial concentration ($p > 0.05$). In the case of zeolite size, values above 0.04 mg/g were only achieved for the $\text{PO}_4^{3-}\text{-P}$ initial concentrations above 10 mg/L, when the medium zeolite size (1.5–3.0 mm) and 20 g of adsorbent (zeolite) were employed. The results suggest that there is no relationship between the zeolite size and the saturation adsorption of $\text{PO}_4^{3-}\text{-P}$ ($p > 0.05$). Therefore, any of the zeolite sizes employed in this study could be used as a support medium in treatment wetlands. Furthermore, when the zeolite amount was increased from 20 g to 50 g (2.5 times), there was no increased effect of the saturation adsorption of $\text{PO}_4^{3-}\text{-P}$. In comparison to results for the $\text{NH}_4^+\text{-N}$ adsorption, this is another difference with the $\text{PO}_4^{3-}\text{-P}$ adsorption onto natural zeolite.

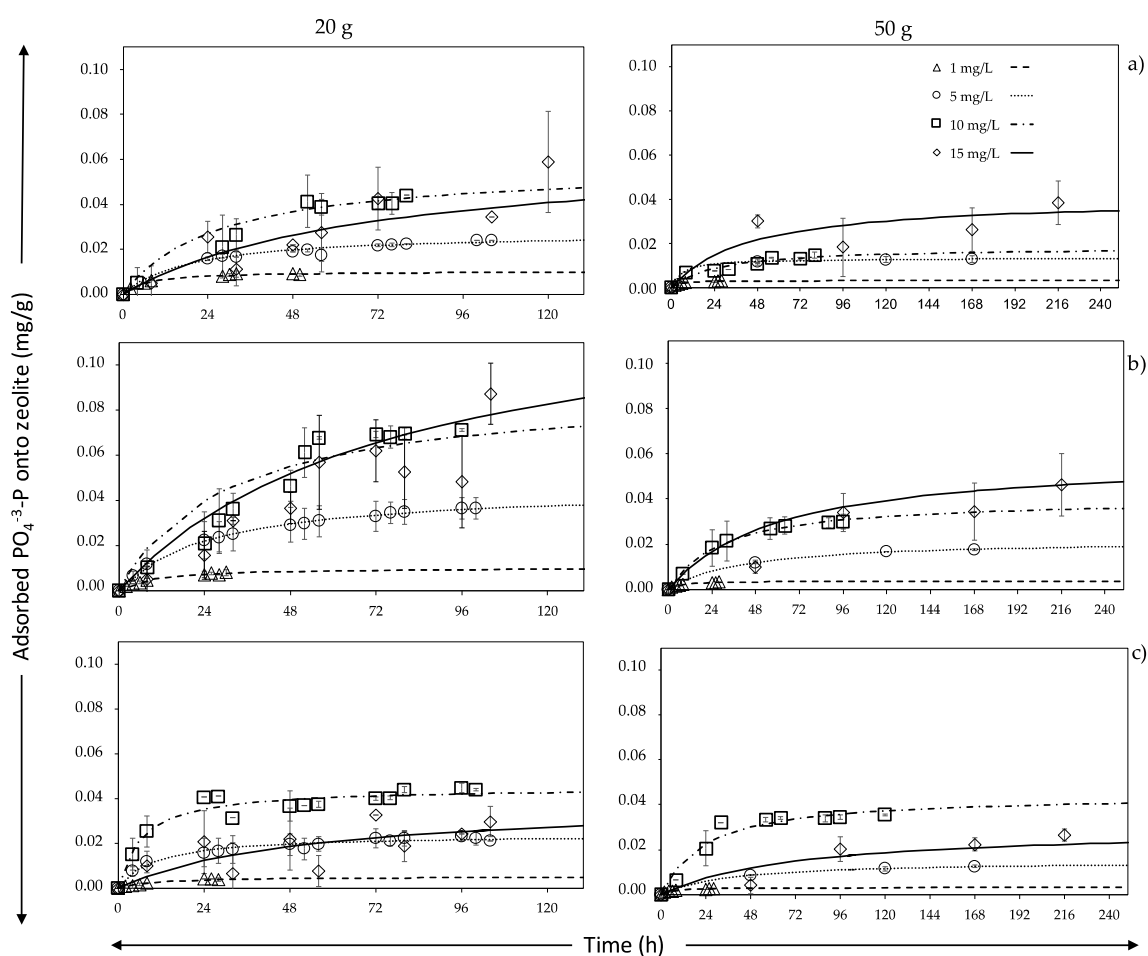


Figure 2. Adsorbed phosphate (mg/g) onto zeolite vs. time in batch assays for the determination of adsorption characteristics. Particle size: (a) 5.0–8.0 mm; (b) 1.5–3.0 mm; and (c) 0.2–1.0 mm.

Additionally, for adsorption capacity, Table 4 shows the $\text{NH}_4^+\text{-N}$ and $\text{PO}_4^{3-}\text{-P}$ removal percentage measured in the batch assays. Table 4 shows the $\text{NH}_4^+\text{-N}$ removal efficiency above 60%, indifferent to the initial concentration, zeolite size, and zeolite quantity. However, when zeolite sizes are between 1.5 and 3.0 mm, better removal is seen. In the case of $\text{PO}_4^{3-}\text{-P}$, Table 4 shows that the removal efficiency was above 35%, regardless of the initial concentration, zeolite size, and zeolite quantity. $\text{NH}_4^+\text{-N}$ and $\text{PO}_4^{3-}\text{-P}$ removal was always above 70% for zeolite size between 1.5 and 3.0 mm.

Table 4. Percentage of NH_4^+ -N and PO_4^{3-} -P adsorbed onto the zeolite during batch assays for the determination of adsorption characteristics (average $\pm$ standard deviation).

Batch Assay	Zeolite Amount (g)	Particle Size (mm)	NH_4^+ -N Initial Concentration (mg/L)	NH_4^+ -N Percentage onto Zeolite (%)	PO_4^{3-} -P Initial Concentration (mg/L)	PO_4^{3-} -P Percentage onto Zeolite (%)
1	20	5.0–8.0	85	79.6 $\pm$ 0.6	15	58.6 $\pm$ 0.0
			65	90.8 $\pm$ 0.5	10	43.9 $\pm$ 0.0
			45	94.9 $\pm$ 0.5	5	46.1 $\pm$ 0.0
			25	94.1 $\pm$ 0.3	1	76.4 $\pm$ 0.0
2	50	5.0–8.0	85	95.8 $\pm$ 1.2	15	63.9 $\pm$ 32.5
			65	95.4 $\pm$ 4.0	10	37.2 $\pm$ 3.5
			45	94.6 $\pm$ 0.6	5	63.1 $\pm$ 8.2
			25	93.5 $\pm$ 4.6	1	78.4 $\pm$ 0.0
3	20	1.5–3.0	85	91.6 $\pm$ 1.7	15	79.5 $\pm$ 0.0
			65	93.0 $\pm$ 2.3	10	71.2 $\pm$ 0.7
			45	94.1 $\pm$ 0.5	5	70.2 $\pm$ 9.0
			25	89.6 $\pm$ 0.6	1	80.7 $\pm$ 13.7
4	50	1.5–3.0	85	95.2 $\pm$ 0.5	15	77.0 $\pm$ 23.2
			65	96.0 $\pm$ 1.0	10	76.3 $\pm$ 8.4
			45	96.3 $\pm$ 0.5	5	85.4 $\pm$ 1.4
			25	93.4 $\pm$ 0.6	1	89.2 $\pm$ 0.0
5	20	0.2–1.0	85	65.4 $\pm$ 6.0	15	55.7 $\pm$ 4.8
			65	66.5 $\pm$ 5.3	10	44.1 $\pm$ 0.7
			45	71.1 $\pm$ 2.5	5	40.7 $\pm$ 0.0
			25	74.2 $\pm$ 1.2	1	37.0 $\pm$ 6.9
6	50	0.2–1.0	85	63.4 $\pm$ 2.5	15	44.2 $\pm$ 4.6
			65	75.1 $\pm$ 2.7	10	90.7 $\pm$ 0.7
			45	81.4 $\pm$ 1.2	5	61.2 $\pm$ 2.8
			25	83.4 $\pm$ 1.2	1	78.4 $\pm$ 0.0

3.2. Adsorption Modelling

From the results presented in Figures 1 and 2, Table 5 shows the results for the adjustment to the saturation-growth-rate model proposed by Equation (1). R^2 and R^2_{adj} are similar as the data number considered in the curve fit increases. In Table 5, the time for $t_{\text{max}/2}$ in the NH_4^+ -N adsorption process had variability, with values from 0.2 h to 7.7 h. Furthermore, the $t_{\text{max}/2}$ was reduced when zeolite quantity increased from 20 g to 50 g for all zeolite sizes evaluated in this work (Table 5). In the case of PO_4^{3-} -P, the time for $t_{\text{max}/2}$ in the PO_4^{3-} -P adsorption process had huge variability, similar to the NH_4^+ -N adsorption process, with values from 5.1 h to 78.2 h. Similar results were achieved for different zeolite sizes evaluated in this work, when zeolite quantity increased from 20 g to 50 g. The time needed for maximum adsorption and removal of compounds of interest from aqueous solutions is an important parameter, because this information would be relevant for determining the recommendations for hydraulic retention time when this material is used as a support medium in treatment wetlands. The m_{max} values were similar for NH_4^+ -N adsorption between different zeolite sizes and quantities but better results for PO_4^{3-} -P adsorption were achieved for zeolite sizes of 1.5–3.0 mm, with values up to 0.14 mg/g when zeolite quantity was 20 g and up to 0.06 mg/g when zeolite quantity was 50 g. These maximum values for the medium size, 1.5–3.0 mm, represent up to three times the m_{max} values of other zeolite sizes. Thus, this result explains that the best removal efficiencies are achieved by the medium zeolite size of 1.5–3.0 mm, as shown in Table 4.

Table 5. Saturation-growth-rate parameters for $\text{NH}_4^+\text{-N}$ and $\text{PO}_4^{3-}\text{-P}$ adsorption onto zeolite.

Batch Assay	Particle Size (mm)	Zeolite Amount (g)	$\text{NH}_4^+\text{-N}$ Initial Concentration (mg/L)	$m_{\max}$ (mg/g)	$t_{\max/2}$ (h)	R^2_{adj}	$\text{PO}_4^{3-}\text{-P}$ Initial Concentration (mg/L)	$m_{\max}$ (mg/g)	$t_{\max/2}$ (h)	R^2_{adj}
1	5.0–8.0	20	85	0.84	1.0	0.99	15	0.064	68.9	0.89
			65	0.62	0.5	0.99	10	0.057	26.9	0.99
			45	0.57	7.7	0.98	5	0.027	18.9	0.98
			25	0.23	0.7	0.99	1	0.010	6.8	0.98
2		50	85	0.35	0.2	0.99	15	0.041	42.9	0.89
			65	0.25	0.2	0.99	10	0.018	27.6	0.95
			45	0.18	0.7	0.99	5	0.013	6.3	0.99
			25	0.09	0.3	0.99	1	0.003	3.4	0.99
3	1.5–3.0	20	85	0.70	1.9	0.88	15	0.136	78.2	0.96
			65	0.66	1.0	0.99	10	0.090	30.3	0.96
			45	0.46	1.2	0.99	5	0.045	25.6	0.99
			25	0.26	1.1	0.99	1	0.010	9.9	0.99
4		50	85	0.40	3.7	0.99	15	0.059	60.2	0.86
			65	0.26	0.7	0.99	10	0.040	29.7	0.99
			45	0.16	0.4	0.98	5	0.022	40.5	0.99
			25	0.26	0.1	0.99	1	0.004	6.4	0.98
5	0.2–1.0	20	85	0.66	1.4	0.98	15	0.039	52.1	0.67
			65	0.48	1.1	0.97	10	0.045	6.6	0.98
			45	0.36	0.8	0.98	5	0.024	10.6	0.98
			25	0.19	1.0	0.97	1	0.005	10.8	0.99
6		50	85	0.21	0.7	0.98	15	0.030	73.1	0.94
			65	0.20	1.0	0.97	10	0.044	23.0	0.97
			45	0.15	0.7	0.97	5	0.015	36.6	0.99
			25	0.08	0.5	0.97	1	0.003	5.1	0.99

Figure 3 shows the adsorption isotherm for particle size and zeolite amount from the batch assays of the two analyzed compounds: $\text{NH}_4^+\text{-N}$ and $\text{PO}_4^{3-}\text{-P}$. In the case of $\text{NH}_4^+\text{-N}$, Figure 3 shows a typical evolution of the sorption isotherm when 50 g of zeolite was used. For $\text{PO}_4^{3-}\text{-P}$, the sorption isotherm was in the linear phase and the beginning of the saturation phase for the two quantities of zeolite and the different sizes. The result for $\text{PO}_4^{3-}\text{-P}$ shows the potential of the material to be used for treatment of wastewater with concentrations above 15 mg/L and, considering the typical concentrations found in domestic wastewaters, it suggests that it can be used to treat this kind of wastewater.

Table 6 shows the Langmuir adsorption kinetic parameters, calculated by regression using Equation (2) and the coefficient of determination (R^2 and R^2_{adj}), which are based on data from Figure 3. According to results presented in Table 6, all analytical isotherms showed R^2 above 0.9. Despite that, when the zeolite amount of 50 g and particle size of 5.0–8.0 mm were adjusted to the Langmuir model, the maximum adsorption capacity, Q , had a negative value. This result can be explained because the $\text{NH}_4^+\text{-N}$ concentrations evaluated in the batch assays (up to 85 mg/L), for these conditions of quantity and size, were apparently at the start of the linear phase ($b \times \text{Ce} \ll 1$) and not in the saturation phase; thus, the mass of the adsorbate per mass unit of adsorbent at the equilibrium is described by $q = Q \cdot b \cdot \text{Ce}$. This equation has infinite solutions, one of these being a negative slope, as shown in Table 6.

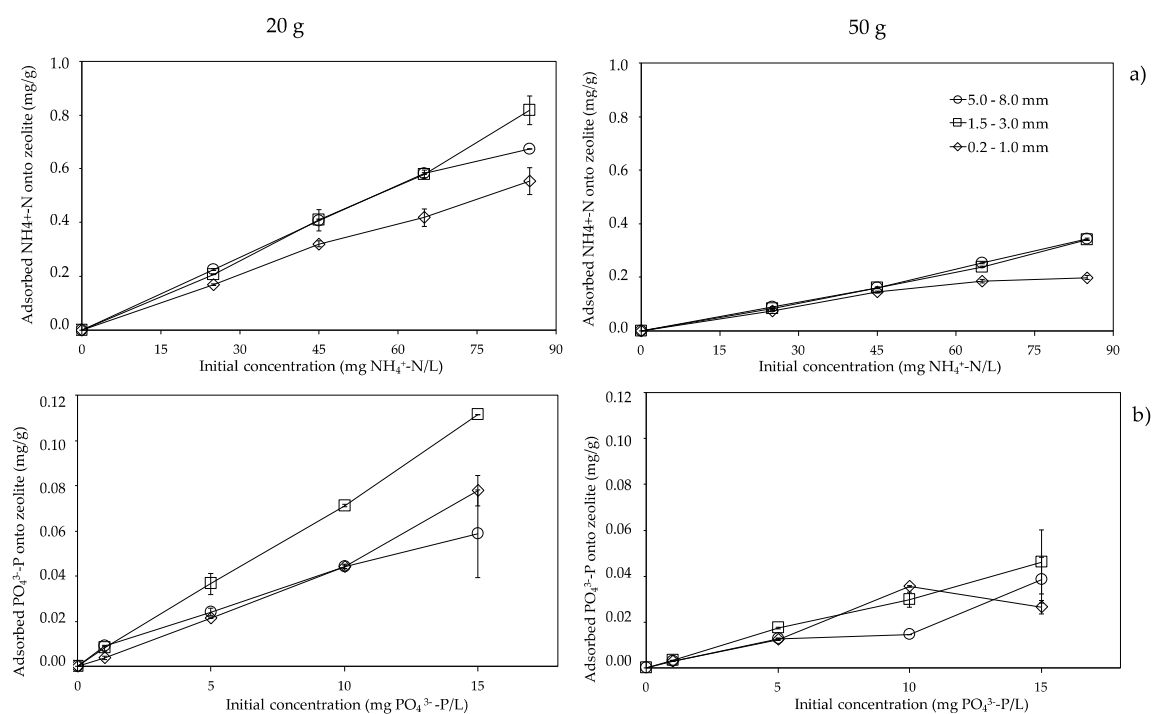


Figure 3. Adsorbed ammonium (mg/g) and phosphate (mg/g) onto zeolite vs. initial concentration in batch assays for the determination of adsorption characteristics. (a) ammonium and (b) phosphate.

Table 6. Langmuir parameters for NH₄⁺-N and PO₄³⁻-P adsorption onto zeolite.

Batch Assay	Compound	Zeolite Amount (g)	Particle Size (mm)	Adsorption Kinetic Parameters		R ²	R ² _{adj}
				Maximum Adsorption Capacity (Q) (mg/g)	Energy for Adsorption (b) (L/mg)		
1	NH ₄ ⁺ -N	20	5.0–8.0	0.93	0.25	0.89	0.78
2		50	5.0–8.0	−0.31	−0.14	0.99	0.98
3		20	1.5–3.0	1.58	0.13	0.99	0.98
4		50	1.5–3.0	0.96	0.13	0.99	0.98
5		20	0.0–1.0	1.13	0.03	0.99	0.98
6		50	0.0–1.0	0.30	0.09	0.99	0.98
1	PO ₄ ³⁻ -P	20	5.0–8.0	0.05	0.79	0.94	0.88
2		50	5.0–8.0	0.03	0.36	0.99	0.98
3		20	1.5–3.0	0.08	0.71	0.97	0.94
4		50	1.5–3.0	0.05	0.92	0.99	0.98
5		20	0.0–1.0	0.17	0.05	0.99	0.98
6		50	0.0–1.0	0.03	0.34	0.99	0.98

Table 6 shows that the medium zeolite size (1.5–3.0 mm) had higher values for the maximum adsorption capacity of ammonium for the two quantities evaluated (20 g and 50 g), above 0.95 mg/g and up to 1.58 mg/g. Similarly, for phosphate, the medium size showed higher values when 50 g were used, above 0.04 mg/g; however, it showed the second highest removal when 20 g were used, with removal above 0.08 mg/g. These results explain why the best removal results were achieved for this size of zeolite, as shown in Table 4.

4. Discussion

The behavior of the adsorption process of NH_4^+ -N and PO_4^{3-} -P could be described for Chilean natural zeolites through two adsorption models: Saturation-growth-rate and Langmuir (Table 5, Figure 3, Table 6). The results are similar to the results reported for other materials studied to be used as support mediums in treatment wetlands [9,32,53]. In addition, the results of this study confirm that Chilean natural zeolites can be used for both N and P removal from wastewater (including those produced in rural areas) and that their potential application as a support medium for treatment wetlands is similar to that of other natural zeolites previously used for this purpose [30,40,54].

Of the different zeolite sizes evaluated, the medium size of 1.5–3.0 mm was the size that performed best, achieving an NH_4^+ -N removal above 85% and a PO_4^{3-} -P removal above 70% (Table 4). The removal efficiencies achieved with this size show that adsorption can be improved for both NH_4^+ -N and PO_4^{3-} -P removal by at least 40% and 30%, respectively, in comparison to traditional support mediums, such as sand and gravel, which have a more limited capacity [5,21]. In addition, the highest maximum adsorption capacity of NH_4^+ -N was achieved for this zeolite size (1.5–3.0 mm), with values up to 1.6 mg/g. However, the regular values reported for the NH_4^+ -N maximum adsorption capacity varied between 2.7 and 31 mg/g [22]. According to this, the NH_4^+ -N maximum adsorption capacity of this study is around 60% of the minimum value reported in the literature. However, the result achieved in this work (1.58 mg/g) shows that Chilean natural zeolite has the potential to remove ammonium from wastewater (Table 4).

For PO_4^{3-} -P, the medium zeolite size (1.5–3.0 mm) showed the highest maximum adsorption capacity, with values up to 0.08 mg/g. The potential capacity is three times better than the results reported by Andrés et al. [10], with 0.026 mg/g for another Chilean natural zeolite and 1.0–2.0 mm size. The difference could be justified by the Ca content and zeolite size and, therefore, the surface area. The Ca content was described by Del Bubba et al. [55] as an important factor that influences the P adsorption capacity in natural materials employed as adsorbents. In this work, the reported Ca content was 3.42%, while in Andrés et al. [10] it was 2.5%. With respect to size, the P adsorbed is expected to increase as the adsorbent surface increases [56,57], as is the case when the zeolite size decreases because there is a larger contact surface available.

However, Moharami and Jalali [32] showed that, when the adsorbent quantity and surface are greater, there is a very fast adsorption onto the adsorbent surface and the consequence is a lower adsorbate concentration in the solution. The result is that some adsorption sites on the adsorbent surface remain unsaturated. Therefore, the adsorbate concentration in the solution drops to a lower value, which makes it possible that the amount of adsorbate per unit weight of adsorbent can be reduced when the adsorbent quantity and surface are increased.

According to Table 3, the $t_{\text{max}/2}$ for the 1.5–3.0 mm zeolite size varies from 0.1 to 2 h for NH_4^+ -N removal and from 6.0 h up to 80 h (approximately 3 d) for PO_4^{3-} -P removal. This result can be seen in the need for longer hydraulic retention time (HRT) in treatment wetlands to reach 50% of the maximum adsorption capacity of the tested zeolite. In the case of treatment wetlands with horizontal subsurface-flow (HSSF-TWs), the HRT varies from 1.5 to 7 d [58]; thus, residence time considered in the present study is included. In the case of treatment wetlands with vertical subsurface-flow (VSSF-TWs), the HRT is short and under one day [59]; thus, NH_4^+ -N removal can be achieved but it might not be enough for PO_4^{3-} -P removal. However, the HRT in VSSF-TWs can be increased by saturating the bottom of the bed [60].

The lifespan of the zeolite (up to saturation) as a support medium in a SSF-TW for wastewater treatment is an important aspect that can be assessed by determining the adsorption maximum capacity achieved by adsorption experiments. In wastewater, one person produces around 2 g P/PE-d and 12 gN/PE-d [61]. Therefore, according to the study, 12.5 g of the Chilean natural zeolite would be necessary for P and N removal. Considering that the design recommendation for HSSF-TWs include 5 m^2 /PE and depth of 0.5 m [62], then 2.5 m^3 of volume or 5500 kg of zeolite (density of zeolite, 2200 kg/m^3 , Engler and Rubio [29]) would be necessary for the support medium. This quantity of HSSF-TWs would

be useful for 611 d (almost 2 years). This can be considered a low lifespan. However, Andrés et al. [10] showed that a material such as the natural zeolite can extend the lifespan of the SSF-TW up to 2 times through the regeneration of adsorption sites as a result of the plants' uptake of nutrients and aeration strategies. Thus, the lifespan of the Chilean zeolites studied indicates that they have the potential to be used for longer periods of time than those calculated only by the adsorption process. However, further studies will help determine the duration of this lifespan extension. In a complementary way, Andrés et al. [10] showed that maximum adsorption capacity for P removal was increased by ten times when tested by batch loading the assays, when zeolite was the unique support medium in SSF-TWs for wastewater treatment. This increase in maximum adsorption capacity, under real operation, can be explained by the more adsorbent surface available for adsorption as a consequence of more zeolite employed in SSF-TWs. In addition, Drizzo et al. [63] attributed the increase to the age of the system, hydraulic distribution, pretreatment unit, solids, and plant condition. Milliot et al. [38] employed natural zeolites as a layer of support media in VSSF-TWs for treating wastewater, and discussed reductions in the capacity of ammonium removal. The reductions were explained by the effect of several factors such as preferential flows, short hydraulic residence times, and low concentration of influent ammonium (below 10 mg/L). To solve it: two strategies were proposed: (1) increasing zeolite's quantity, and (2) employing a similar layer, reducing zeolite granulometry to increase the adsorbent surface. Regarding the second solution, this work showed that reducing the granulometry did not necessary redound to the increase of the adsorption capacity (Table 5); the kinetics reaction is more important than mass transfer. Therefore, increasing zeolite quantity in the TW seems to be a better solution because more adsorbent surface is available and therefore the adsorption capacity would increase. Another strategy could be the use of an external filter as post treatment, which would imply the use of an extra structure but might result in long-term operation and maintenance savings. This research can be helpful considering the serious operational problem of SSF-TWS: clogging [64]. Clogging is the accumulation of solids (wastewater suspended solids) or the buildup of biofilm (chemical precipitates, plant detritus accumulation and biofilm growth) that results in porosity and hydraulic conductivity and water transport decrease over time [65]. This problem could affect the contact time between zeolite and wastewater; thus, reducing the removal capacity of ammonium and phosphate by the SSF-TWs during the treatment. However, different management strategies to reduce clogging in SSF-TWs are discussed in Nivala et al. [66], where the authors suggest a limit of 250 g/m² for cross-sectional Biological Oxygen Demand (BOD) loading. In recognition of the physical reality that most SSF treatment wetland processes are a function of biofilm surface area, Austin et al. [67] propose a method to systematically analyze this type of clogging as a design tool: A Damköhler number (Da) definition based on aggregate specific surface area is used to investigate a method of predicting clogging induced by heterotrophic biofilms growing on treatment media.

Finally, taking into account the previous discussion, the Chilean natural zeolite with a commercial size of 1.5–3.0 mm is recommended to be used as the support media in treatment wetlands to remove N and P from domestic wastewaters, including those produced in rural areas. In addition, after saturation in treatment wetlands, the Chilean natural zeolite has the possibility to be used as a source of nutrients, namely N and P, as has already been proposed by several authors [27,68–70].

5. Conclusions

A new material, Chilean natural zeolite, for the removal of ammonium and phosphate from wastewaters, including those produced in rural areas, was described in this work. The saturation-growth-rate equation was fit successfully to the experimental data to determine the adsorption rate for each batch assay. On the other hand, the adsorptions of NH₄⁺-N and PO₄³⁻-P were described for the Langmuir isotherm and the results showed that the commercial zeolite size of 1.5–3.0 mm was the size that had better adsorption behavior for NH₄⁺-N and PO₄³⁻-P, with maximum adsorption capacities up to 1.58 mg/g and 0.08 mg/g, respectively, as well as the greatest potential for the removal of these elements contained in wastewater. These results show that these two compounds

can be removed from aqueous solutions using Chilean natural zeolite and the material has the potential to be used for the removal of NH_4^+ -N and PO_4^{3-} -P from rural wastewater. Therefore, Chilean natural zeolite has the potential to be used as a support medium in treatment wetlands, taking advantage of its adsorbent properties. Finally, 12.5 g of the Chilean natural zeolite would be necessary for the removal of P and N found in wastewater in the amount produced by one person every day. Finally, considering the design recommendation for HSSF-TWs for treating wastewater coming from one inhabitant, the zeolite used in this kind of treatment wetland as a support medium would have a lifespan of around two years considering only the adsorption effect.

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