



Characterization and environmental application of a Chilean natural zeolite

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Abstract

The use of natural zeolites for environmental applications is gaining new research interests mainly due to their properties and significant worldwide occurrence. The present work describes the characterization of a natural Chilean zeolite and the results as adsorbent for ammonia from aqueous solutions. The zeolitic-rich tuff sample, mainly composed of clinoptilolite and mordenite, consisted of 13 μm mean volumetric particle diameter, 55 $\text{m}^2 \text{g}^{-1}$ (methylene blue adsorption) and 177 $\text{m}^2 \text{g}^{-1}$ (nitrogen adsorption) of specific surface area. Particles were negatively charged over a broad pH range (with or without ammonia) and 1.02 meq $\text{NH}_4^+ \text{g}^{-1}$ cation-exchange capacity. The ammonia removal appears to proceed through ion-exchange and rapid kinetics (rate constant of 0.3 min^{-1}) at neutral pH value, with removal capacities up to 0.68 meq $\text{NH}_4^+ \text{g}^{-1}$. The Langmuir isotherm model provided excellent equilibrium data fitting ($R^2=0.97$). Results indicate a significant potential for the Chilean natural zeolite as an adsorbent/ion-exchange material for wastewater treatment and water reuse applications.

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1. Introduction

Zeolite minerals, also known as natural sedimentary or natural occurring zeolites (Mondale et al., 1995), are mainly composed of aluminosilicates with a three-dimensional framework structure bearing AlO_4 and SiO_4 tetrahedra. These are linked to each other by sharing all of the oxygen to form interconnected cages and channels containing mobile water molecules and

alkali (sodium, potassium, lithium, and caesium) and/or alkaline earth (calcium, strontium, barium, and magnesium) cations (Tschernich, 1992). These exchangeable cations give rise to the ion-exchange properties of the material.

Only a few of the existing natural zeolites in the world are found in sufficient quantity and purity as required by industry. Within this group, silica-rich heulandite (clinoptilolite) and mordenite are the most important and play a significant industrial role (Mondale et al., 1995; Tschernich, 1992). Important uses of zeolite minerals include water softening, gas and petroleum processing, mining, sewage treatment, paper products, among others (Tschernich, 1992). Main

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URL: <http://www.lapes.ufrgs.br/laboratorios/ltn/ltn.html>.

Table 1
Environmental applications of natural zeolites

Wastewater treatment	References
Ammonia removal	Baykal (1998), Cincotti et al. (2001), Demir et al. (2002), Dyer and White (1999), Hlavay et al. (1982), Jorgensen and Weatherley (2003), Klieve and Semmens (1980), Langella et al. (2000), Mercer et al. (1970), Rozic et al. (2000)
Heavy metals removal	Bosso and Enzweiler (2002), Cincotti et al. (2001), Inglezakis et al. (2001), Kesraoui-Ouki et al. (1994), Langella et al. (2000), Mondale et al. (1995), Panayotova (2001)
Organic compounds removal	Garcia et al. (1993), Li et al. (2000)
Radioactive elements removal	Abusafa and Yucel (2002), Dyer and Zubair (1998)

reported environmental applications and related studies, particularly in wastewater treatment, are summarised in Table 1.

The excessive presence of ammonia in water streams and effluents is a problem of great concern for the environment and industrial water systems, mainly due to eutrophication and corrosion/biological fouling problems, respectively (Mercer et al., 1970; Rozic et al., 2000). Existing methods and technologies for the removal of this pollutant/contaminant, i.e. biological and physicochemical, are constantly being either adapted or improved and recent efforts have been made to discover new economically feasible and environmentally friendly alternatives (Rozic et al., 2000). In this context, the use of natural zeolite for the removal of highly loaded ammonia bearing wastewater appear to have potential due to the advantages and peculiarities over some conventional and expensive ion-exchange resins (Demir et al., 2002; Mercer et al., 1970).

Zeolitic-rich tuffs have been studied for the removal of ammonia from aqueous solutions, including material from Hungary (Hlavay et al., 1982), Turkey (Demir et al., 2002), Croatia (Rozic et al., 2000), USA (Klieve and Semmens, 1980), Italy (Cincotti et al., 2001; Langella et al., 2000) and other countries (Dyer and White, 1999). Yet, the number of studies reported on the use of natural zeolites from South America is evident in only a few publications (Bosso and Enzweiler, 2002). Thus, studies of characterization and applications (especially environmental ones) of such

minerals available in South America should be of great importance to that region.

Thus, the main objective of this work is to describe the characterization of a natural zeolitic-rich tuff from Chile (Minera Formas™) and to evaluate the use as an ion-exchange material for the removal of ammonia from aqueous solutions.

2. Experimental

2.1. Materials and reagents

A Chilean natural zeolite (designated here as “Ch-zeolite”), from an important and abundant mine in Chile, was provided by Minera Formas™. The sample was homogenized and sieved below 149 μm (100 Mesh Tyler™) before characterization and experimentation. Main physical, mineralogical and chemical properties are summarised in Tables 2 and 3.

Synthetic ammonia solutions were prepared with (NH₄)₂SO₄ (analytical purity) for the determination of the cation-exchange capacity of the Ch-zeolite and ion-exchange batch experiments. Methylene blue (C₁₆H₁₈N₃SCI·3H₂O) of analytical purity and ultra pure (>99.999%) nitrogen gas (N₂) were used for surface area determination of the Ch-zeolite. Analytical purity sodium chloride (NaCl) was used for chemical modification of the Ch-zeolite in the determination of its cation-exchange capacity. The pH adjustments for the ion-exchange batch experiments were made using H₂SO₄ and NaOH solutions. Analytical purity potassium nitrate (KNO₃) was used in the zeta potential measurements of the Ch-zeolite. The pH adjustments for zeta potential measurements were made using HNO₃ and KOH solutions. All solutions were prepared with deionised water.

Table 2
Main characteristics of the Ch-zeolite

Cation-exchange capacity (meq g ⁻¹)	2.05
Specific gravity (g cm ⁻³)	2.2
Mineralogical composition	Clinoptilolite (48%), Mordenite (30%), Albite (5%) and Quartz (15%)
Particles size	100% below 149 μm (100 Mesh Tyler™)

Data kindly provided by Minera Formas™.

2.2. Methods

Chemical analysis. Ammonia concentration was determined using a titrimetric method, with a preliminary distillation step, based on the *Standard Methods for the Examination of Water and Wastewater* (APHA, 1995). The results are expressed as $\text{mg NH}_3\text{-N l}^{-1}$.

Methylene blue concentration was determined using a photometer (Merck™ SQ 118) at 660 nm, and compared to a linear standard calibration curve. Results are expressed in mg l^{-1} .

2.2.1. Physical and physicochemical characterization

The particle size distribution of the Ch-zeolite was determined using a laser diffraction equipment (CIL-AS™ 1064) and standard wet sieving (Mesh Tyler™ series).

Scanning electron microscopy (SEM-PHILIPS™ XL20) was used for photomicrographs as well as to analyse the Ch-zeolite composition (Energy Dispersion X-ray, EDX). The sample was initially placed in a vacuum chamber for coating with a thin layer (few nanometers) of gold (Au).

The specific surface area of the material was measured by the methylene blue technique and by nitrogen gas adsorption methods, with the latter also providing information about particle porosity.

In the methylene blue adsorption method, aqueous solutions (50 ml) of methylene blue (100 mg l^{-1}) were agitated using an orbital shaker (Marconi™) for an hour at room temperature in the presence of different quantities of the Ch-zeolite (0.05–0.3 g). The suspensions were then allowed to settle for 23 h and the resulting supernatants were centrifuged at 5000 rpm before the analysis of the residual methylene blue concentration. Results obtained correspond to averaged values of three different experiments. The specific surface area was evaluated by the Langmuir model, assuming the formation, at high concentrations, of a dye monolayer and $1.08 \text{ nm}^2 \text{ molecule}^{-1}$, for the cross-sectional area (Van den Hul and Lyklema, 1968).

The Ch-zeolite specific surface area was evaluated by the nitrogen gas adsorption method, using automated equipment (Autosorb 1-Quantachrome Instruments™), employing multipoint BET isotherm adsorption data fitting. Also from these data, the porosity of the material was evaluated through parameters such as volume of total pores ($d < 206 \text{ nm}$),

surface area and volume of micropores ($d < 2 \text{ nm}$; Micropore Analysis Method).

Zeta potential measurements for the natural and ammonia loaded zeolite, as a function of medium pH, were determined using a Zeta Plus™ equipment (Brookhaven Instruments). Suspensions (0.01% v/v) of the Ch-zeolite, previously sieved below $37 \mu\text{m}$ (400 Mesh Tyler™), in a $10^{-3} \text{ mol l}^{-1}$ solution of KNO_3 were used and the medium pH was controlled with the addition of HNO_3 ($\text{pH} < 7$) and KOH ($\text{pH} > 7$), separately. For the Ch-zeolite saturated with ammonia, suspensions of the material were prepared by the same procedure, except that the sample was loaded with $100 \text{ mg NH}_3\text{-N l}^{-1}$ of ammonia.

The water content of the zeolite mineral was evaluated by gravimetric means. A sample of the material was dried in a laboratory furnace (373 K) for 24 h, cooled in a desiccator and its mass was monitored in a precision balance ($\pm 0.1 \text{ mg}$). The difference between the dried mass value and the equilibrium mass value was used to evaluate the moisture content.

The cation-exchange capacity of the zeolite mineral was determined by chemical modification with NaCl . A known quantity of the material (5 g) was contacted with 50 ml of a NaCl 1 M solution for 24 h at room temperature and the suspension was agitated in a glass flask using an orbital shaker (Marconi™). Then, the suspension was filtrated and washed three times with 100 ml deionised water. The wet modified material was dried at room conditions for 48 h and used further in agitated flasks experiments for ammonia removal studies. Tests were conducted with 0.25 g of Ch-zeolite, 100 ml of $100 \text{ mg NH}_3\text{-N l}^{-1}$ solution, for 2 h, using the same procedure as in the ion-exchange experiments.

2.2.2. Ion-exchange studies

Batch ion-exchange experiments were carried out in agitated glass flasks (100 ml). In the kinetic studies, the system containing a suspension (0.25 g of zeolite + 100 ml of a $100 \text{ mg NH}_3\text{-N l}^{-1}$ solution) was agitated at room temperature in the orbital shaker for different periods of time.

The ammonia uptake isotherms were measured using a similar procedure during 120 min (sufficient for attaining chemical equilibrium) and varying the feed solution concentrations. Then, suspensions were

filtered in a membrane filter (mean pore diameter of 0.45 μm), and the resulting solutions were analysed for pH and ammonia concentration.

The effect of medium pH was studied adjusting the pH before agitation in the orbital shaker. All ion-exchange results were averaged values of duplicate tests.

The ammonia uptake (q), expressed as ammonia removal per unit mass of Ch-zeolite ($\text{mg NH}_3\text{-N g}^{-1}$), was calculated according to Eq. (1), where C_0 is the initial ammonia concentration ($\text{mg NH}_3\text{-N l}^{-1}$), C_f is the final ammonia concentration ($\text{mg NH}_3\text{-N l}^{-1}$), V is the batch volume (l) and m is the Ch-zeolite mass (g).

$$q = \frac{(C_0 - C_f) \cdot V}{m} \quad (1)$$

A simple first order kinetic model for a reversible reaction, given by Eq. (2), was used to describe the kinetic data obtained, as commonly used for ion-exchange and adsorption onto natural materials (Bereket et al., 1997; Panayotova, 2001). The parameters k' and C_{eq} in Eq. (2) are, respectively, the overall rate constant (min^{-1}) and the equilibrium concentration ($\text{mg NH}_3\text{-N l}^{-1}$).

$$-\frac{dC_f}{dt} = k'(C_f - C_{\text{eq}}) \quad (2)$$

Langmuir and Freundlich models, given by Eqs. (3) and (4), respectively, were used to describe the equilibrium data (isotherm) obtained. Langmuir parameters q_{max} ($\text{mg NH}_3\text{-N l}^{-1}$) and K ($\text{l mg}^{-1} \text{NH}_3\text{-N}$) from Eq. (3) are the monolayer capacity attained at high concentrations and the equilibrium constant, respectively (Perry and Green, 1999). Freundlich parameters K_F ($\text{mg NH}_3\text{-N g}^{-1} (\text{l mg}^{-1} \text{NH}_3\text{-N})^{1/n}$) and $1/n$ (–) from Eq. (4) are the Freundlich capacity factor and the Freundlich intensity parameter, respectively (Weber, 1972).

$$q = \frac{q_{\text{max}} K C_f}{1 + K C_f} \quad (3)$$

$$q = K_F C_f^{1/n} \quad (4)$$

Langmuir and Freundlich data fitting were done by linearisation of Eqs. (3) and (4), given by Eqs. (5) and (6), respectively.

$$\frac{C_f}{q} = \frac{1}{K \cdot q_{\text{max}}} + \frac{1}{q_{\text{max}}} C_f \quad (5)$$

$$\log q = \log K_F + \frac{1}{n} \log C_f \quad (6)$$

3. Results and discussions

3.1. Characterization

The particle size distribution of the zeolite, obtained by means of laser diffraction method, is shown in Fig. 1.

The mean particle diameter (volumetric) obtained was about 13 μm , and the results from sieve analysis showed approximately the same particle size distribution for the Ch-zeolite. This size distribution favours the kinetics of the ion-exchange process because, in general, the rate of exchange is proportional to the inverse of the square of the particle diameter (Tchobanoglous et al., 2003).

Photomicrographs of the Ch-zeolite sample, obtained by SEM, are shown in Figs. 2 and 3.

The qualitative composition analysis (EDX) obtained for the grain shown in Fig. 3 can be seen in Fig. 4.

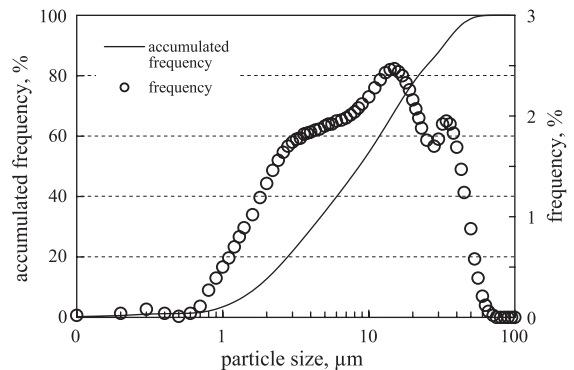


Fig. 1. Particle size distribution of the Ch-zeolite.

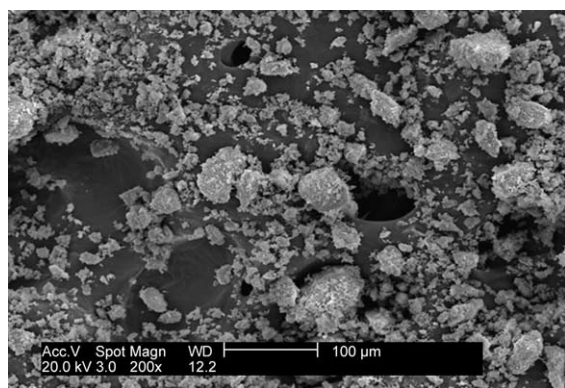


Fig. 2. Typical topographic image for the original Ch-zeolite by Scanning electron photomicrographs (SEM). Bar length is 100 μm and the magnification 200 \times .

Fig. 4 shows, apart from the gold (Au) peak, that the main chemical elements (Al, Si, O, Na, Mg, K, Ca and Fe) are present in the structure of this natural zeolite, in agreement with the structure of this natural zeolite, in agreement with the chemical composition (Table 3).

The specific surface area determined by methylene blue adsorption method was about $55 \text{ m}^2 \text{ g}^{-1}$ and equilibrium data and Langmuir data fitting obtained for this measurement are shown in Fig. 5.

According to Fig. 5, the maximum uptake of methylene blue, from aqueous solutions, by the Ch-zeolite was about 27 mg g^{-1} , showing a high adsorbing capacity for this type of dye material.

The specific surface area determined by nitrogen gas adsorption (BET model) was found to be 177 m^2

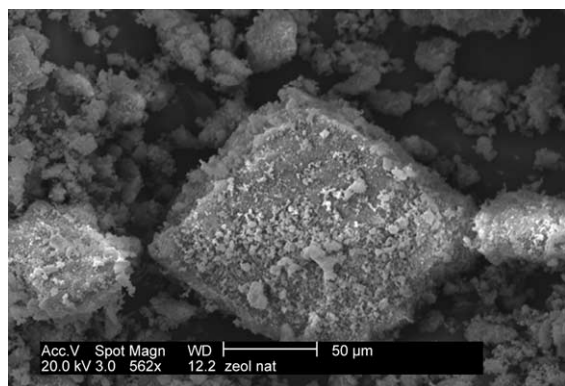


Fig. 3. Image of a grain Ch-zeolite by SEM. Bar length is 50 μm and the magnification 562 \times .

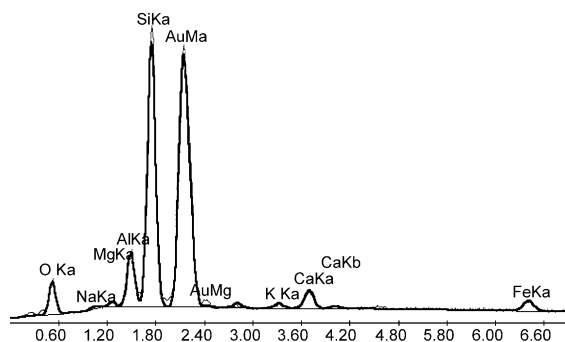


Fig. 4. Scanning electron spectral analyses of a Ch-zeolite grain (see Fig. 3).

g^{-1} . According to Da Luz (1995), values of specific surface area for clinoptilolite and mordenite are usually of the order of 300 and $400 \text{ m}^2 \text{ g}^{-1}$, respectively. The results obtained for the material porosity showed a total volume pore ($d < 206 \text{ nm}$) of $0.26 \text{ cm}^3 \text{ g}^{-1}$, micropore ($d < 2 \text{ nm}$) volume and surface area of 0.043 and $69 \text{ m}^2 \text{ g}^{-1}$, respectively.

The apparent conflicting results in the values obtained for the specific surface area by the methylene blue and nitrogen adsorption methods can be explained by the molecular cross-sectional areas of the adsorbates (N_2 : $0.162 \text{ nm}^2 \text{ molecule}^{-1}$; methylene blue: $1.08 \text{ nm}^2 \text{ molecule}^{-1}$). These values make the accessibility, within the porous internal structure, very different. More, as many different studies have shown, specific surface area measurements are usually dependent on the selected method and experimental conditions yielding, very often, erratic values (Ribeiro et al., 2003; Van den Hul and Lyklema, 1968).

Table 3
Chemical composition of the Ch-zeolite

Constituent	%
SiO_2	67.00
Al_2O_3	13.00
TiO_2	0.20
Fe_2O_3	2.00
Na_2O	2.60
K_2O	0.45
CaO	3.20
MgO	0.69
MnO	0.04
P_2O_5	0.05

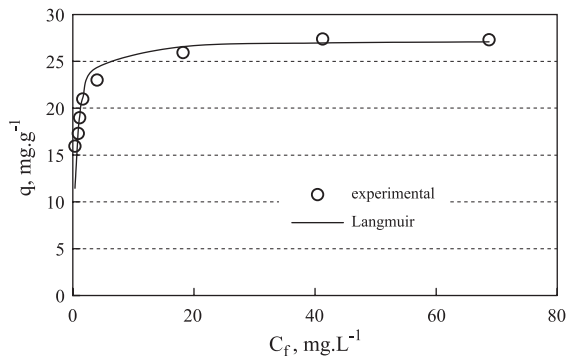


Fig. 5. Equilibrium data (isotherm) of methylene blue adsorption from aqueous solutions by Ch-zeolite for specific surface area measurement. Contact time: 24 h; C_0 : 100 mg l^{-1} ; Temperature: 22°C ; Experimental error: $\pm 0.06 \text{ mg l}^{-1}$.

Zeta potential measurements obtained for the zeolite as a function of medium pH are shown in Fig. 6. Third-order polynomials were used for zeta potential data fitting, giving correlation coefficients (R^2) higher than 0.99.

Results obtained show that zeolite surface groups are mainly negative in the pH range studied and that the ammonia uptake does not interfere much the zeta potential measurements, confirming that the mechanism is not electrostatic (charge neutralization) but a result of an ion-exchange reaction.

The water content of the material (moisture) was of the order of 5% (wt.), after 200 min needed to reach equilibrium with the surrounding atmosphere humidity. This low moisture of the zeolite minimizes the experimental error in cation-exchange capacity determination (weight measurement procedures), making easier the comparison with ion-exchange capacity data reported in the literature (Klieve and Semmens, 1980).

The cation-exchange capacity for the Ch-zeolite, obtained through modification of the natural sample with NaCl (homoionisation), was $18.3 \text{ mg NH}_3\text{-N g}^{-1}$ ($1.02 \text{ meq NH}_4^+ \text{ g}^{-1}$). The results obtained for the natural sample without treatment and the sample washed with deionised water were 13.4 and $15.3 \text{ mg NH}_3\text{-N g}^{-1}$ (0.74 and $0.85 \text{ meq NH}_4^+ \text{ g}^{-1}$), respectively.

The homoionisation of the Ch-zeolite clearly enhances the ammonia uptake capacity by about 37%, what is also observed for the deionised water

washing procedure (14%). The latter is due to surface dust (precipitated salts and other impurities clogging part of the pore openings in the zeolite structure) that is removed from the natural sample during the washing (Inglezakis et al., 2001).

The equivalent-based capacity values were calculated according to the equivalent number of ammonium cations exchanged ($18 \text{ mg NH}_3\text{-N meq}^{-1} \text{ NH}_4^+$), since this is the main ion participating in the reaction (Demir et al., 2002). Results obtained are similar to the values found in the literature for other commercially available natural zeolites and ion-exchange materials used in ammonia removal applications (Klieve and Semmens, 1980; Tchobanoglous et al., 2003). Despite the increase in the uptake capacity, the treatment and modification (“activation”) of the Ch-zeolite as an ion-exchange material must undergo an economical and environmental analysis of the actual benefits.

3.2. Ion-exchange studies

Results from batch ion-exchange experiments with different pH values of the suspension (zeolite + ammonia solution) are shown in Table 4.

Results indicate an optimal pH value of 6 (near neutrality) for ammonia removal by the zeolite. Yet, according to the equilibrium Bronsted–Lowry acid–base reaction, given by Eq. (7) (Russel, 1992), the ammonia removal should be greater at lower pH values and smaller at higher pH values, if the cat-

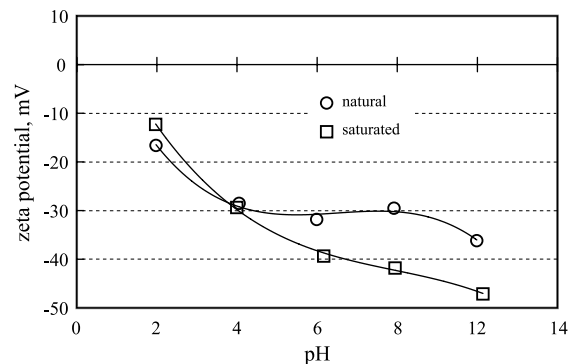


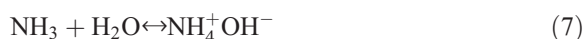
Fig. 6. Zeta potential of the Ch-zeolite and the Ch-zeolite saturated with ammonia (Zeolite: 0.22 g l^{-1} ; C_0 : $100 \text{ mg NH}_3\text{-N l}^{-1}$ and $10^{-3} \text{ mol l}^{-1}$ solution of KNO_3) Experimental error: $\pm 3.0 \text{ mV}$.

Table 4
Influence of pH in the removal of ammonia from aqueous solutions by Ch-zeolite ion-exchange

pH	q (mg NH ₃ -N l ⁻¹)
4	10.6
6	11.5
9	8.9

C_0 : 100 mg NH₃-N l⁻¹; Contact time: 120 min; Zeolite: 2.5 g l⁻¹; Temperature: 22 °C; Experimental error: ± 1 mg NH₃-N l⁻¹.

ion-exchange mechanism occurs only by means of the ammonium ion (NH₄⁺) (Demir et al., 2002).



However, the slightly lower capacities results obtained under low pH conditions may be due to H⁺-NH₄⁺ competition for the exchange sites in the zeolite surface (Inglezakis et al., 2001), as can be seen in the chemical diagram constructed for a 100 mg NH₃-N l⁻¹ (0.00552 mol NH₃-N l⁻¹) aqueous solution system (Fig. 7). In addition, the ammonia uptake is drastically reduced at pH values higher than 9 when, according to this figure, the NH₃ gaseous species begin to be significant. Results obtained at neutral pH are convenient for the process in terms of effluent emission.

The kinetic data for the ammonia removal process is illustrated in Fig. 8, which includes a first order reversible reaction modelling. The overall rate constant k' (Eq. (2)) obtained from such fitting was 0.3 min⁻¹, indicating a rapid approach to chemical equilibrium (approximately 15 min). This is particularly important in continuous process operation, because lower resident times are required to reduce footprint installations using compact units.

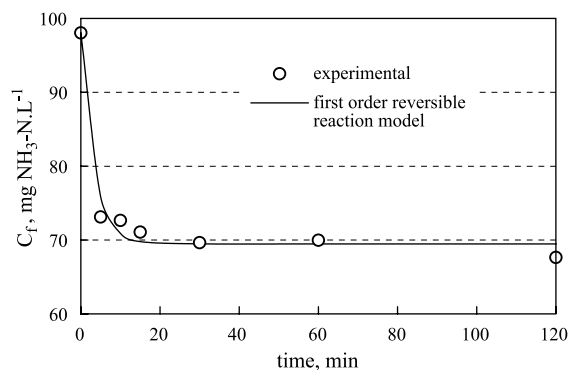


Fig. 8. Kinetics of ammonia removal from aqueous solutions by Ch-zeolite ion-exchange. Zeolite: 2.5 g l⁻¹; Temperature: 25 °C; pH: 5.8 \pm 0.2; Experimental error: ± 1 mg NH₃-N l⁻¹.

Similar kinetic results were obtained by Demir et al. (2002) with a clinoptilolite from Turkey (particle size range: 125–1000 μm), where contact times between 5 and 15 min were found sufficient to reach equilibrium (C_0 : 10–80 mg NH₃-N l⁻¹).

The isotherm obtained from agitated flasks studies is shown in Fig. 9, together with the corresponding Langmuir (Eq. (3)) model values.

The Langmuir model provided excellent correlation of the experimental equilibrium data (Fig. 9), yielding correlation coefficient values of $R^2 = 0.9741$,

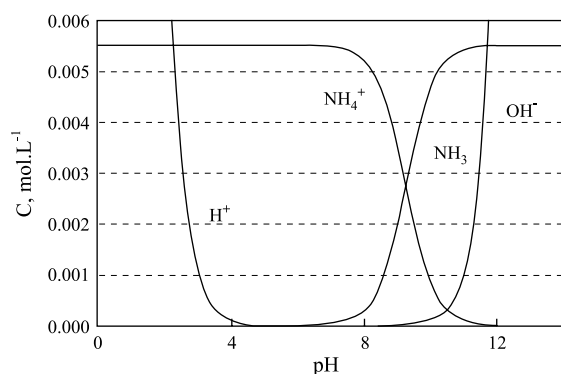


Fig. 7. Chemical diagram species for ammonia aqueous solution.

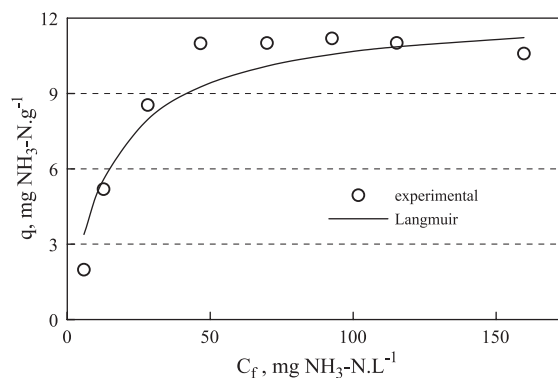


Fig. 9. Equilibrium data (isotherm) of ammonia removal from aqueous solutions by the Ch-zeolite. Contact time: 120 min; Zeolite: 2.5 g l⁻¹; Temperature: 24 °C; pH: 5.8 \pm 0.2; Experimental error: ± 3 mg NH₃-N l⁻¹.

Table 5
Summary of results—characterization and ammonia removal studies

Chilean natural zeolite (Ch-zeolite)	
Mean particle volumetric diameter (μm)	13
Specific surface area—methylene blue ($\text{m}^2 \text{g}^{-1}$)	55
Specific surface area— N_2 ($\text{m}^2 \text{g}^{-1}$)	177
Total pore volume with diameter less than 206 nm ($\text{cm}^3 \text{g}^{-1}$)	0.26
Pore volume with diameter less than 2 nm—micropores ($\text{cm}^3 \text{g}^{-1}$)	0.043
Specific surface area—micropores ($\text{m}^2 \text{g}^{-1}$)	69
Zeta potential (mV)	–20 to –40
Cation-exchange capacity (meq $\text{NH}_4^+ \text{g}^{-1}$)	1.02
Ammonia removal—optimal pH	6
Ammonia removal—overall rate constant (min^{-1})	0.3
Ammonia removal—maximum uptake (meq $\text{NH}_4^+ \text{g}^{-1}$), Langmuir model	0.68

compared to results for the Freundlich model where $R^2 = 0.805$. From the Langmuir parameters calculated, the maximum uptake of ammonia (q_{max}) by Ch-zeolite ion-exchange is $12.3 \text{ mg NH}_3\text{-N g}^{-1}$ ($0.68 \text{ meq NH}_4^+ \text{g}^{-1}$). Equilibrium data with a suitable mathematical description of results is of great importance in the design of ion-exchange processes (Perry and Green, 1999).

The main results obtained in the present work are summarised in Table 5.

4. Conclusions

This work shows physical, mineralogical and physicochemical data of a Chilean natural zeolitic-rich tuff sample, composed mainly by clinoptilolite and morденite. The sample presented fairly high specific surface area, negatively charged zeta potential and $1.02 \text{ meq NH}_4^+ \text{g}^{-1}$ cation-exchange capacity. The ammonia removal proceeds very rapidly (rate constant of 0.3 min^{-1}) through an ion-exchange mechanism at neutral pH values decreasing at $\text{pH} > 9$ when gaseous NH_3 species begin to form. The Langmuir isotherm model provided best correlation of the equilibrium data ($R^2 = 0.97$) reaching saturation values at $0.68 \text{ meq NH}_4^+ \text{g}^{-1}$. Results obtained indicate significant potential for the Chilean natural zeolite as an adsorbent/ion-

exchange material for wastewater treatment and water reuse applications.

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