**The effects of hydraulic loading and NaCl concentrations on the regeneration of exhausted
homoionic natural zeolite**

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ABSTRACT

A study of the suitable operational conditions for the regeneration of exhausted homoionic natural zeolite with ammonium was carried out. Laboratory-scale columns using NaCl solutions with concentrations of 2 and 4 mol/L and hydraulic loadings of 4, 6 and 8 bed volumes per hour (BV/h) were assessed. For both NaCl concentrations studied, the hydraulic load of 6 BV/h showed the highest ammonia nitrogen output from the exhausted zeolite bed. Results showed that the hydraulic load (BV/h) had a greater influence on the regeneration efficiency than the

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concentration of the regenerating solution.

Keywords: Ammonia nitrogen removal, ion exchange, exhausted homoionic zeolite, chemical regeneration.

INTRODUCTION

The intensive use of land for agriculture and animal breeding has led to an increase in the eutrophication of lakes, estuaries and rivers, and the contamination of underground water reservoirs as a result of the presence of nitrogen, phosphorus and carbon compounds. The continuous increase in the nutrient concentration in different sources of water has led to the introduction of strict regulations for the control of the disposal of nitrogen and phosphorus in different regions.^[1-6] Many wastewater treatment systems do not allow the removal and recovery of nutrients, and final effluents are disposed containing nitrogen and phosphorus compounds. Different methods have been developed for removing ammonia nitrogen from sewage, agricultural and industrial wastes. Among the most widely used methods for removing ammonia from wastewaters are air stripping, ionic exchange and biological nitrification/denitrification. Many researchers concluded that ion exchange is a very promising technology for ammonia nitrogen removal, because of the low investment involved, the appropriateness in extreme climatic conditions (low temperature) and the small area needed for the process.^[7-12]

Ion exchange using different types of natural and synthetic zeolites has been widely employed for ammoniacal nitrogen removal.^[13-16] Several studies on ammoniacal nitrogen sorption capacity of natural zeolite (clinoptilolite and mordenite types) have shown values of between 4 - 20 mg NH₄⁺/g of zeolite.^[14,15,17-19] Studies exist on the optimization of the ion

exchange process using a natural zeolite (clinoptilolite) for ammonia removal. Approximately 50% to 60% of the total cost of the ion exchange process is determined by the chemical regeneration process of the zeolite. In general, hydraulic loads from 4 to 20 bed volumes per hour (BV/h) have been used previously to regenerate ammonium exhausted zeolite.^[18-26] However, no sound study on the influence of the operational conditions for achieving a maximum chemical regeneration of the zeolite has been reported to date.

The aim of the present work was to study the influence and interaction between the hydraulic loading (BV/h) and concentration of the backwash regeneration solution on chemical regeneration of zeolite in order to obtain the most practical and effective regeneration conditions of the zeolite for its reuse.

MATERIALS AND METHODS

Homoionic Natural Zeolites

The natural zeolite used in the experiments was obtained from the Oaxaca deposit in Mexico. The chemical composition of this zeolite was: SiO₂, 58.05%; Al₂O₃, 11.94%; Fe₂O₃, 4.36%; MgO, 0.77%; CaO, 5.94%; Na₂O, 1.5%; K₂O, 1.2%; Ignition Wastes, 12.09%. In addition, its phase composition was: Clinoptilolite, 35%; Mordenite, 15%; Montmorillonite, 30%; Others (Calcite, Feldespathite and Quartz): 20%.

This zeolite was transformed into sodium homoionic zeolite by using a 1 M NaCl solution at approx. 90°C for 2h. This treatment was repeated twice to force the zeolite as far as possible into the relevant homoionic form. The samples treated in this way were washed with deionized water and subsequently dried at 50°C.^[26, 27]

The cationic composition of natural and homoionic zeolites was as follows (all amounts expressed as mg of cation per g of zeolite):

Natural zeolite: Na^+ , 4.6; Ca^{2+} , 16.0; K^+ , 15.6; Mg^{2+} , 8.5.

Homoionic zeolite: Na^+ , 36.8; Ca^{2+} , 2.0; K^+ , 11.7.

The zeolite packed had 58% porosity and an apparent density of 0.81 g/mL. The natural zeolite had a particle size of between 1.0-2.0 mm.

Load and Regeneration Solutions

Ammoniacal influent feed was made from 0.01g/L NH_4NO_3 stock solution. The average value of the ammonia concentration in the influent was 120 mg/L. Regeneration solutions with concentrations of 2 and 4 mol/L (M) NaCl were prepared with deionized water.

Experimental Procedure

Packed columns 20 cm high and with an internal diameter of 3.5 cm were used. They contained a total zeolite mass of 55 g. Ammoniacal influent (NH_4NO_3 solution) was pumped at 2 BV/h and both regeneration solutions (2 and 4 mol/L NaCl) were used at flows of 4, 6 and 8 BV/h.

To obtain the best regeneration conditions, different load-regeneration cycles were applied in order to determine the loss of the ammonium capacity of packed homoionic zeolite. In all experiments, triplicate samples of effluents were taken each hour to determine the required parameters.

Analytical Techniques

Ammonia nitrogen was analyzed by selective electrode (ORION pH/ISE-meter 727). Sodium concentration was determined by Atomic Absorption Spectrometry. Both determinations were carried out following Standard Methods.^[28]

Zeolite samples with a maximum weight of 0.5 g were digested in a microwave oven (CEM Corporation-MDS 2000). Afterwards, the sodium and ammonium contents of the liquid were also determined. This treatment aimed to characterize the zeolite after its regeneration.

RESULTS AND DISCUSSION

The relationship between the hydraulic loading (BV/h) and concentration or molarity of the backwash regeneration solution was determined in order to calculate the operation time needed and to obtain optimal operating conditions. Ammonium removal from zeolite as $(C_o - C_i)/C_o$ for both regeneration solutions (2 and 4 mol/L) applied at different hydraulic loads (BV/h) (Figs. 1 and 2, respectively), where C_o denotes the ammonium concentration in the exhausted zeolite (22.51 mg/g of zeolite) and C_i is the ammonium concentration at any time during the regeneration operation.

In the case of 2 mol/L NaCl solution and 6 BV/h of hydraulic loading, 60% regeneration was obtained at 4 h contact time, whereas 8 h of operation time was needed to obtain similar efficiency at 4 BV/h. Finally, for 8 BV/h only 48% regeneration was reached after 12 h of operation time (Fig. 1).

For 4 mol/L of the regenerating solution and hydraulic loading of 6 BV/h (Fig. 2), 60% regeneration was achieved in the first hour of operation and a maximum of 80 % was obtained at

8 h operation time. By comparing the hydraulic loads of 4 and 8 BV/h, the behaviour was only slightly different during the first five hours of operation. In both cases the systems achieved equilibrium at 9 h operation time with a regeneration percentage of 65%. For both concentrations and similar hydraulic loadings the curves showed a tendency to reach equilibrium at between 8 and 10 hours operation time. At 4 mol/L of regenerating solution and at 4 BV/h, equilibrium was achieved at 3 h, while at other hydraulic loadings 8 hours were needed. For all hydraulic loadings applied with 2 mol/L concentration solutions equilibrium was obtained after 10 h. At 4 mol/L of regenerating solution and hydraulic loading of 4 BV/h, equilibrium was achieved before of comparing to 6 and 8 BV/h regeneration curves.

Lower concentrations of the regenerating solutions (0.5 mol/L, NaCl) and higher flow-rates of these solutions (15-20 BV/h) were previously used to reduce ammonia concentration in regeneration solution effluent to below 0.5 mg $\text{NH}_4^+\text{-N/L}$.^[18] Low concentration of the regenerating solution (0.1 mg/L, NaHCO_3) was also used during the desorption of uranium (VI) in fixed bed ion-exchange columns using natural zeolite coated with Manganese oxide (MOCZ). The column could be used for at least four adsorption-desorption cycles using the above-mentioned NaHCO_3 solution concentration.^[29] Loadings of 7-8 BV/h of a regenerating solution of NaCl were also used for eliminating more than 95% of adsorbed ammonium ions in bench-scale packed zeolite columns. The adsorption-regeneration time ratio was approximately 5:1.^[30]

In all systems studied in the present work, the first two-hour operation appears to have a great influence on the overall kinetics since the relationships between sodium and ammonium concentrations in the liquid-solid interface are the highest. In order to demonstrate this, a mass balance for determining the leached ammonium for hydraulic loadings of 6 and 8 BV/h was carried out with a regenerating solution concentration of 4 mol/L. Figure 3 presents the variation of the accumulative ammonium concentration leached in this experiment with the operation time;

different responses were observed during the first 30 min. A higher concentration of ammonium in the leachate was found in the effluent solution obtained at 6 BV/h than at 8 BV/h. At 1.5 hours of operation time the leachate concentrations were 0.9 mg/L and 0.7 mg/L for 6 and 8 BV/h, respectively, indicating an influence of liquid velocity only during the first hour of operation time. This behaviour could be determined by the fact that at 8 BV/h the diffusion in zeolite structure could be affected by a higher linear velocity applied to the system. Diffusion may be the controlling step in this process, and consequently further ionic exchange sites to solid-liquid interface could not be reached.^[19, 31-35] Overall rates of adsorption, desorption and ion exchange in porous materials are generally controlled by mass transport within the pore network, rather than by the kinetics of desorption or ion exchange itself.^[32] Actually, the effective diffusion coefficient is a macroscopic average over a large number of ions (or molecules) in pores of different sizes, shapes and directions and at larger and smaller distances from the pore walls, expressing the average ability of the species to make headway in any given direction. Limited data are also available on the rates of some metal exchanges on zeolite, in terms of diffusion coefficients.^[32]

Based on the results obtained in the present work, the values of the diffusion coefficients were determined for all conditions studied according to the model described previously by Roque.^[31] These values were summarized in Table 1. For a same hydraulic loading, the diffusion coefficient corresponding to the lowest NaCl concentration (2M) was always higher than that corresponding to the highest concentration used (4 M), especially in the case of a hydraulic load of 4 BV/h.

The values of the diffusion coefficients obtained in this work were somewhat higher than those obtained in the lead uptake process by using clinoptilolite with particle sizes in the range of 0.02-0.045 cm.^[31]

Table 2 summarizes the zeolite characteristics after the regeneration step. The sodium concentration in the zeolite increased with the concentration of regenerating solution. Analyzing the load effect at the same concentration of regenerating solution, it was observed that operating the systems at 6 BV/h only half the time is needed to reach 60% removal as compared to 4 BV/h, while at 8 BV/h the required operation time was more than three times higher. As a consequence, the required NaCl consumption was higher as the operation time increased.

When the systems were fed with 4 M solutions the operation times were shorter and the regeneration efficiencies were maximized, but this also implies an economic analysis. Based on the last results, different load-regeneration cycles were carried out at 6 BV/h hydraulic loading, for both NaCl concentrations. Figure 4 shows the cyclic behaviour of nitrogen and sodium content in the packed zeolite column between each load (with an ammonium solution of 120 mg/L - impair)-regeneration (with both NaCl solutions - pair) cycle.

Despite the cyclic behaviour shown, the ion concentration in the zeolite denotes a slight diminution of both sodium and ammonium between each cycle (load-regeneration). From the second regeneration cycle the breakthrough load point was two hours lower than the first ammonium load, and for the third and fourth cycles four and six hours lower, respectively. This could be due to zeolite loss caused by mechanical shut-down forces and to the pH and conductivity values of regenerating solutions. This phenomenon was also previously observed during a study of regeneration step optimization,^[23] which implied the substitution of 5% zeolite mass column between four and six months, depending on the regeneration step frequency.

Effluent regenerating analysis showed sodium concentration values of 44 ± 3 and 84 ± 2 g/L, for 2 and 4 M respectively, from the fourth-hour of operation time. In the case of ammonium, the values were lower than 85 and 72 mg/L, for 2 and 4 M NaCl solutions respectively. Then, taking into account the ammonium quantity in the regenerating solution output it is possible to suggest

the recirculation of regenerating effluent from a fourth-hour operation time. Besides, it is also necessary to find a sustainable alternative for disposing of this high ammonium content effluent, according to the geographical location where the technology is being applied.

CONCLUSIONS

A higher influence of the hydraulic loading of the regeneration solution than of the concentration of this solution on the regeneration efficiency was found. For a hydraulic loading of 8 BV/h a considerable diminution in the regeneration efficiency was observed. The cyclic behaviour of different load-regeneration showed a slight progressive decrease in the zeolite capacity. Therefore, it is very important to consider putting back the material of exchange due to the capacity lost during the process.

REFERENCES

- [1] Fai, G.; Geyer, J.; Okun, D. Purificación de aguas y tratamiento y remoción de aguas residuales. Ingeniería Sanitaria y de Aguas Residuales Vol. 2, Primera parte. 4th ed, **1987**, pp. 217-273.
- [2] Hobson, P.N.; Robertson, A.M. Waste treatment in Agriculture, Applied Science Publishers, London, **1977**.
- [3] Taiganides, E.D. Animal Wastes, Elsevier, London, **1977**.
- [4] Gomes-Ferreira, J.; Bricker, S.B.; Castro-Simas, T. Application and sensitivity testing of an eutrophication assessment method on coastal systems in the United States and European Union. J. Environ. Manage. **2007**, 82, 433-445.

- 218 [5] Mao, J.; Chen, O.; Chen, Y. Three dimensional eutrophication model and
219 application to Taihu Lake, China. *J. Environ. Sci.* **2008**, *20*, 278-284.
- 220 [6] Kotta, J.; Kotta, I.; Sunm, M.; Pollupüü, M. Separate and interactive effects of
221 eutrophication and climate variables on the ecosystem elements of the Gulf of
222 Riga, Estuarine. *Coast Shelf Sci.* **2009**, *84*, 509-518.
- 223 [7] Panayotova, M.; Velikov, B. Influence of zeolite transformation in a homoionic
224 form on the removal of some heavy metal ions from wastewater *J. Environ. Sci.*
225 *Health part A.*, **2003**, *38*, 545-554.
- 226 [8] Armagan, B. Factors affecting the performances of sepiolite and zeolite for the
227 treatment of textile wastewater. *J. Environ. Sci. Health part A.*, **2003**, *38*, 883-896.
- 228 [9] Tobinaga, T.; Shoji, R. Development of new toxicity identification evaluation by
229 assessing toxicity reduction on adsorption and ion-exchange treatments. *J. Environ.*
230 *Sci. Health part A.*, **2004**, *39*, 2341-2353.
- 231 [10] Wajima, T.; Shimizu, T.; Ikegami, Y. Synthesis of zeolites from paper sludge ash
232 and their ability to simultaneously remove NH_4^+ and PO_4^{3-} . *J. Environ. Sci. Health*
233 *part A.*, **2007**, *42*, 345-350
- 234 [11] Milán, Z.; Montalvo, S.; Ruiz-Nagle, N.; Urrutia, H.; Chamy, R.; Sánchez, E.;
235 Borja, R. Influence of heavy metal supplementation on specific methanogenic
236 activity and microbial communities detected in batch anaerobic digesters. *J.*
237 *Environ. Sci. Health part A.*, **2010**, *45*, 1307-1314.
- 238 [12] Milan, Z.; Montalvo, S.; Ilangoan, K.; Monroy, O.; Chamy, R.; Weiland, P.; Sánchez, E.;
239 Borja, R. The impact of ammonia nitrogen concentration and zeolite addition on the
240 specific methanogenic activity of granular and flocculent anaerobic sludges. *J. Environ.*
241 *Sci. Health part A.*, **2010**, *45*, 883-889.

- 242 [13] Rožić, M.; Cerjan-Stefanović, S.; Kurajica, S.; Vančina, V.; Hodž, E. Ammoniacal
243 nitrogen removal from water by treatment with clays and zeolites. *Water Res.* **2000**, *34*,
244 3675-3681.
- 245 [14] Sanchez, E.; Milan, Z.; Borja, R.; Weiland, P. Piggery waste treatment and nutrient
246 removal by ionic exchange. *Resour. Conserv. Recyc.* **2005**, *15*, 235-244.
- 247 [15] Jung, J.Y.; Chung, Y.C.; Shin, H.S.; Son, D.H. Enhanced ammonia nitrogen removal
248 using consistent biological regeneration and ammonium exchange of zeolite in
249 modified SBR process. *Water Res.* **2004**, *38*, 347-354.
- 250 [16] Karapma, N. Application of natural zeolite for phosphorus and ammonium removal from
251 aqueous solutions. *J. Hazard. Mater.* **2009**, *170*, 1186-1191.
- 252 [17] Booker, N.A.; Cooney, E.L.; Priestley, A.J. Ammonia removal from sewage using natural
253 Australian zeolite. *Water Sci. Technol.* **1996**, *34*, 17-24.
- 254 [18] Du, Q.; Liu, Z.; Cao, Z.; Wang, Y. Ammonia removal from aqueous solution using natural
255 Chinese clinoptilolite. *Sep. Purif. Technol.* **2005**, *44*, 229-234.
- 256 [19] Cooney, E.L.; Booker, N.A.; Shallcross, D.C.; Stevens, G.W. Ammonia removal from
257 wastewaters using natural Australian zeolite. I. Characterization of the zeolite. *Sep. Sci.*
258 *Technol.* **1999**, *34*, 2307-2317.
- 259 [20] Amphet, C.B. *Inorganic Ion Exchanger: The Zeolites*. Elsevier, New York, **1964**.
- 260 [21] Ames, L.L. Zeolitic removal of ammonium ions from agricultural and other
261 wastewater. 13th Pacific Northwest Industrial Waste Conference Proceeding,
262 Washington State University, Pullman, **1967**.
- 263 [22] Mercer, B.W.; Arnett, R.C.; Dean, R.B. Optimization of column
264 performance for ammonia removal from wastewater using selective ion
265 exchange. *Wastewater Reclamation and Reuse Workshop Proceedings, Sanitary*

Engineering Research Laboratory, University of California, Berkeley,
1970, pp. 25-27.

[23] USEPA, Optimization of ammonia removal by ion exchange using
 clinoptilolite. Project No. 17080 DAR. Water Pollution Control Research Series,
 Berkeley, California, USA, **1971**.

[24] Koon, J.H.; Kaufman, W.J. Ammonia removal from municipal wastewater by ion
 exchange. *J. Water Poll. Control Fed.* **1975**, *47*, 448-467.

[25] Semmens, M.J.; Wang, J.T.; Booth, A.C. Nitrogen removal by ion
 exchange: biological regeneration of clinoptilolite. *J. Water Poll. Control Fed.*
1977, *49*, 2431-2444.

[26] Milán, Z.; Sánchez, E.; Weiland, P.; De las Pozas, C.; Borja, R.; Mayari, R.;
 Roviroso, N. Ammonia removal from anaerobically treated piggery manure by ion
 exchange in columns packed with homoionic zeolite. *Chem. Eng. J.* **1997**, *66*, 65-
 71.

[27] Jama, M.A.; Yucel, H. Equilibrium studies of sodium-ammonium,
 potassium-ammonium and calcium-ammonium exchanges on clinoptilolite
 zeolite. *Sep. Sci. Technol.* **1990**, *24*, 1393-1416.

[28] APHA-AWWA-WPCF. Standard Methods for the Examination of Water and
 Wastewater, 17th edition (American Public Health Association), Washington,
1989.

[29] Zou, W.; Zhao, L.; Han, P. Removal of uranium (VI) by fixed bed ion-exchange
 column using natural zeolite coated with Manganese oxide. *Chinese J. Chem. Eng.*
2009, *17*, 585-593.

[30] Liu, C.H.; Lo, K.V. Ammonia removal from compost leachate using zeolite III.

Regeneration of zeolite columns. J. Environ. Sci. Health A **2001**, 36, 1825-1843.

[31] Roque, R. Física química de las zeolitas. CNIC, Editorial Pueblo y Educación, 1st. Edition. C. Habana, Cuba, **1988**.

[32] Inglezakis, V.J.; Diamandis, N.A.; Loizidou, M.D.; Grigoropoulou, H.P. Effect of pore clogging on kinetics of lead uptake by clinoptilolite. J. Colloid Interf. Sci. **1999**, 215, 54-57.

[33] Inglezakis, V.J.; Loizidou, M.D.; Grigoropoulou, H.P. Equilibrium and kinetic ion exchange studies of Pb^{2+} , Cr^{3+} , Fe^{3+} and Cu^{2+} on natural clinoptilolite. Water Res. **2002**, 36, 2784-2792.

[34] Dyer, A.; White, K.J. Cation diffusion in the natural zeolite clinoptilolite. Thermochim. Acta **1999**, 340, 341-348.

[35] Karger, J. Measurement of diffusion in zeolites - A never ending challenge. Adsorption **2003**, 9, 29-35.

FIGURE CAPTIONS

Figure 1. Time course of zeolite regeneration using a 2 mol NaCl/L solution with different loads (BV/h).

Figure 2. Time course of zeolite regeneration using a 4 mol NaCl/L solution with different loads (BV/h).

Figure 3. Accumulative ammonium concentration leached at hydraulic loadings of 6 and 8 BV/h.

Figure 4. Variation of the amount of ammonium and sodium chloride exchanged in miliequivalents during the loading and regeneration cycles, respectively.

Fig. 1

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Fig. 2

Fig. 3

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Fig. 4

Table 1. Values of the diffusion coefficients (De , cm²/s)* obtained for all the experimental conditions tested.

Operational conditions (Load and NaCl conc.)	De (cm ² /s)
4BV/h and 2 mol/L	4.5×10^{-8}
4BV/h and 4 mol/L	0.6×10^{-8}
6BV/h and 2 mol/L	2.9×10^{-8}
6BV/h and 4 mol/L	2.3×10^{-8}
8BV/h and 2 mol/L	2.4×10^{-8}
8BV/h and 4 mol/L	1.8×10^{-8}

* The standard deviations of the diffusion coefficient values were less than 5% in all cases.

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445 **Table 2.** Results of the zeolite features after its regeneration.

Condition (Load and NaCl conc.)	mg of Na ⁺ /g of zeolite &	Breakthrough removal percent	t _{60%} (h) &&	Required g of Na ⁺ (*)
4BV/h and 2 mol/L	33.09	60	8	88.73
4BV/h and 4 mol/L	34.55	60	1.5	35.04
6BV/h and 2 mol/L	31.73	60	4	74.89
6BV/h and 4 mol/L	34.01	60	0.88	28.48
8BV/h and 2 mol/L	29.76	50 (**)	15 (**)	374.03
8BV/h and 4 mol/L	33.66	60	3	150.7

446 (*) Based on 60% removal of ammonia nitrogen from zeolite bed.

447 (**) Obtained from curve extrapolation.

448 & Values of sodium concentration in the zeolite were averages of three determinations; the
449 standard deviations of the mean values were less than 5% in all cases.

450 && t_{60%}: time (h) that is necessary to reach 60% ammonium removal or 60% zeolite
451 regeneration.