INVESTIGATION OF CLINOPTILOLITE NATURAL ZEOLITE REGENERATION BY AIR STRIPPING FOLLOWED BY ION EXCHANGE FOR REMOVAL OF AMMONIUM FROM AQUEOUS SOLUTIONS

[1]A.R. Rahmani, *[1]M.T. Samadi, [2]H.R. Ehsani

[1] Department of Environmental Health Engineering, Faculty of Public Health and Center for Health Research, Hamadan University of Medical Sciences, Hamadan, Iran
[2] Department of Environmental Health Engineering, School of Public Health, Hamadan University of Medical Sciences, Hamadan, Iran

Received 9 November 2008; revised 20 June 2009; accepted 2 August 2009

ABSTRACT
The purpose of this study was to regenerate clinoptilolite natural zeolite by air stripping followed by removal of ammonium from aqueous solutions. The research was carried out in continuous system. The characteristics of graded clinoptilolite from Semnan (one of the central provinces in Iran) mines were determined and then regeneration tests were done by contacting of 1 N NaCl solution with given weights of ammonium saturated zeolite. Then the brine of column was transferred to the air stripping column for regeneration. The pH of brine solution before entrance to a stripping column was increased to 11. Air stripped ammonia from the brine was converted to the ammonium ion by using acid scrubber. The outlet effluent from stripping column was collected for reuse. The results showed that the cation exchange capacities were 17.31 to 18.38 mg NH_4^+/g of zeolite weight. Regeneration efficiency of zeolite by NaCl solution and air stripping was in the range of 92%-97% under various operational conditions. However, the efficiency of acid absorption of released ammonia in stripping process was 55% with a major rejection of the surplus ammonia to the atmosphere. It could be concluded that the method studied may be considered as an advanced and supplementary process for treating effluents of aqueous solution and fishponds in existing treatment plants.

Key words: Ammonium removal, Ion exchange, Clinoptilolite natural zeolite, Air stripping, Regeneration

INTRODUCTION
Presence of ammoniacal nitrogen (ammonia and ammonium) in municipal, industrial and agricultural wastewaters promotes eutrophication of receiving waters and is potentially toxic to fish and other aquatic life (Nguyen and Tanner, 1998; Emadi, 2001). When ammonia accumulates to toxic levels, fish cannot extract energy from feed efficiently. If the ammonia concentration becomes high enough, the fish will become lethargic and eventually fall into a coma and die. In properly managed fishponds, ammonia seldom accumulates to lethal concentrations. Of particular concern are the deleterious effects that inorganic forms of nitrogen (nitrate, ammonia, and nitrite) exert on human health. If nitrate is reduced to nitrite and ammonia by natural or artificial processes, it posses a serious public health threat, especially for very young infants (Hargreaves and Tucker, 2004). For drinking water, the USEPA has set the maximum contaminant level (MCL) at 1 mg NO_2–N/L. However, Iranian current regulation shows the MCL at 1.5 mg NH_3-N/L. Nitrate and ammonia stimulates the excessive growth of algae and other unwanted aquatic plants. They also have harmful effects on aquatic wildlife directly through toxic effects or indirectly by oxygen depletion.

Ammonia in water is either unionized ammonia

*Corresponding author: *samadi@umsha.ac.ir*
Tel: +98 811 8260661

(NH_3) or the ammonium ion (NH_4^+). The relative proportion of the two forms in aqueous solutions is mainly affected by pH. Un-ionized ammonia is the more toxic form and predominates when pH is high (Tchobanoglouss *et al*., 2003). Ammonium ion is relatively nontoxic and predominates when pH is low. In general, less than 10% of ammonia consists the toxic form when pH is <8. However, this proportion increases dramatically as pH increases (Hargreaves and Tucker, 2004)

The three most widely used methods for removing ammonium from polluted waters are Air Stripping (AS), Ion Exchange (IE) and biological nitrification-denitrification (Tchobanoglouss *et al*., 2003). Clinoptilolite is a natural zeolite(Z) that has been known for its ability to remove ammonium from polluted waters by ion exchange (Emadi *et al*., 2001; Tchobanoglouss *et al*., 2003; Farkas *et al*., 2005). The capacity of zeolite and chemical regeneration for ammonium removal has been investigated in several studies (Ershov, 1984; Haralambous *et al*., 1992; Kazemian, 1993; Celik *et al*., 2001 ; Demir *et al*., 2002; Rahmani *et al*., 2004; Du Q *et al*., 2005). Usually, the service cycle is a down flow packed-bed column followed by chemical regeneration (usually by NaCl). This process is carried out in two separate phases (Semmens and Porter, 1979; Lahav and Green, 1998):

Ion exchange stage: A column filled with zeolite is used for NH_4^+ IE from secondary effluent. When NH_4^+ concentration breakthrough occurs, the regeneration stage after backwashing the bed is started.

Regeneration stage: contacting zeolite and brine solution in a column system. A cation containing solution is recirculated through the bed in order to desorb NH_4^+ of the solution as follows:

$$Z\text{-}NH_4^+ + Na^+ \longleftrightarrow Z\text{-}Na^+ + NH_4^+ \qquad (1)$$

The major drawback of this process is the high cost of the chemical regeneration stage including treatment and disposal of the concentrated ammonium-sodium brine produced (Celik *et al*., 2001). Hence, there is a strong cost incentive to look at improving the technique for regeneration the zeolite.

During the last years several investigators have studied other methods of regeneration of IE systems (Semmens and Porter, 1979; Lahav, and Green, 1998; Rahmani and Mahvi, 2006). In these researches, the mechanism of regeneration was IE followed by nitrification.

The purpose of this study was to remove NH_4^+ ions from secondary effluent by IE and regeneration of clinoptilolite natural zeolite by air stripping.

During the regeneration stage, the effluent contains the displaced NH_4^+ ions. Ammonia can be removed from the effluent by converting NH_4^+ ions to NH_3, by raising pH, and then release of NH_3 by passing the effluent through an air-stripping tower. A packed tower is used with a countercurrent of air drawn through bottom openings (Corbitt, 1999; Roberts and Alley, 2000) .

$$NH_4^+ \longleftrightarrow NH_3 + H^+ \qquad (2)$$

The suggested processes may have several advantages in comparison to the IE-AS process including high reaction rate, good control of effluent quality and non sensitivity to fluctuation of ammonium concentration. The result of this regeneration process would be the accumulation of brine for further clarification and reuse.

MATERIALS AND METHODS

The clinoptilolite natural zeolite in rock form was supplied from Semnan mines (in the center part of Iran). The collected samples of zeolite were grounded and sieved and the fractions between U.S. standard mesh numbers of 20 and 30 (0.84 and 0.589 mm) were applied. The zeolite samples after being washed for removing fines were conditioned. For conditioning of zeolite, 0.25 M ammonium sulfate and 1 M sodium chloride solutions were contacted for 24 h. in separate stages with zeolite samples. Then the samples were rinsed with deionized water and stored dry.

Description of applied pilot system

The system was composed of the following items: Two columns made of Plexiglass with L=100cm and an ID=5.5cm as IE; a feeding pump; a centrifugal recirculation pump and a pH meter. The IE columns were filled with 250g of conditioned clinoptilolite natural zeolite in two mesh sizes of 20 and 30 and the bed volume was obtained from 275 to 266 mL, respectivly. Another column was made of plexiglass (with L=90 cm and ID=6.3 cm) used as an AS tower. For increasing the contact between the effluent and air, the column was filled with 200 small rubber balls. The packed tower was applied with a countercurrent of air through bottom openings. Air was supplied by an air compressor at 150 to 220 L/hr in the reactor. The temperature of reactor was controlled at 29±2 ^{o}C with an immersion heater. The pilot is shown schematically in Fig 1.

Determination of clinoptilolite natural zeolite capacity

Ammonium chloride stock solution was prepared by dissolving 1 g NH_4Cl in 1 liter of deionized water. For preparation of the synthetic samples, appropriate amounts of ammonium chloride stock were added to distilled water to give 40 mg/L ammonium concentration and then passed through the column by gravity feed constant head device with 12 BV/h (Bed Volume per hour). The pH of the inlet solution to IE column was adjusted at 7 with manual addition of 1M NaOH solution. The ammonium content of the effluent was measured at the outlet of the colomn. Service cycle was stopped when the ammonium concentration increased to 2 mg/L. The obtained breakthrough curve was used to calculate the capacity of the zeolite for ammonium exchange. The column was then regenerated with 1M NaCl solution (brine ; pH=7) at 10 BV/h. The regenerant solution was passed through the column in upflow mode. The absence of NH_4^+ in the effluent indicated the completion of regeneration. All analysis were made according to the Standard Methods (APHA, 1998).

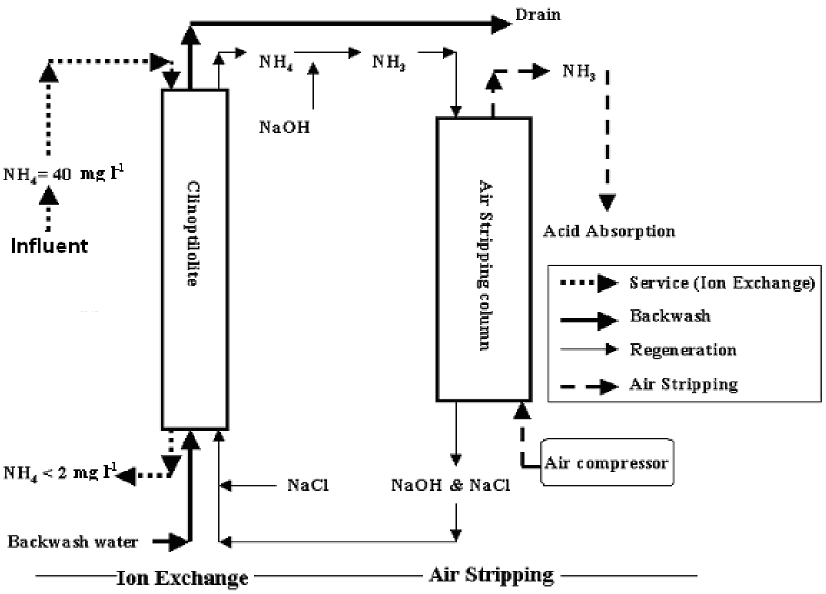

Fig. 1: Schematic diagram of designed pilot

Regeneration of effluent by air stripping

In the beginning of regeneration phase, the ammonium-saturated IE column was backwashed with water for 5 minutes at approximately 30 percent expansion. The clinoptilolite natural zeolite was regenerated by recirculating 1 M NaCl solution (brine) through the column. The brine from storage tank (20 L) was pumped upflow through the IE column and then recirculated to the AS tank. A variable speed pump recirculated the effluent at 10 BV/h and fluidized the bed to 20% expansion. The brine in contact with clinoptilolite eluted ammonium ions were transferred to the AS column for the stripping of NH_3. The pH of the regenerant solution before entrance to AS column was increased up to 9 and 11, respectively, with manual addition of 1M NaOH solution.

The effluent from regeneration stage of IE column was sprayed downflow to the AS reactor. NH_3

was absorbed into the air from the water surface. Then NH_3 stripped from the brine was converted to ammonium ion using acid scruber (500 mL of 1N HCl solution). The outlet brine from AS column was collected in storage tank for reuse (Fig 1).

The ammonium concentration of the brine storage tank and AS outlet was measured during the regeneration phase. The amount of absorbed ammonium in acid was measured at the end of the test. Then the IE column was backwashed and replaced in service.

RESULTS

Charactristics of clinoptilolite natural zeolite

The breakthrough curves for ammonium removal by clinoptilolite for 12 BV/hr of the aqueous solution are shown in Fig. 2, which presents the complete regeneration with 1M NaCl solution. Ammonium elution by regenerant solution is shown in Fig. 3, which describes that a volume of 2.5 liter of 1M NaCl solution is sufficient for nearly complete regeneration of the zeolite column. The results indicated that high level of regeneration (96.9%-97.7%) might be achieved by applying NaCl solution (Table 1).

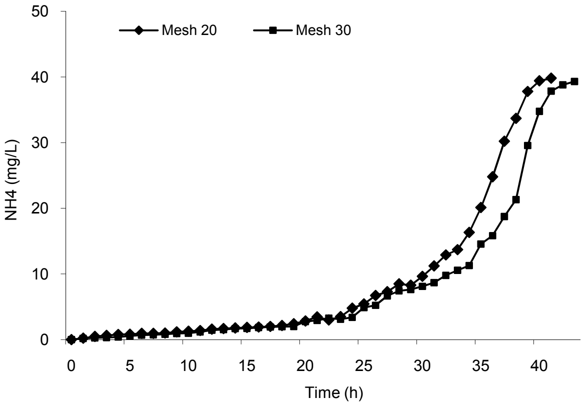

Fig. 2: Clinoptilolite capacity measurements recorded as mg of NH_4^+/g of dry clinoptilolite in continuous system

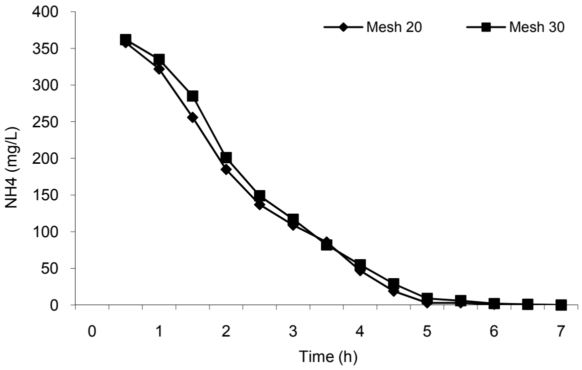

Fig. 3: Ammonium elution by regenerant solution (1M ClNa) in column system

Table 1: Semnan clinoptilolite natural zeolite capacity charactristics

	Mesh 20	Mesh 30
Ammonium concentration, C_0 , mg/L	40	40
Breakthrough capacity , mg NH_4^+/g zeolite	9.61	10.06
Total capacity, mg NH_4^+/ g zeolite	17.31	18.38
Total ammonium adsorbed in column, mg	4327	4595
Total ammonium released in regeneration, mg	4197	4491

Regeneration of ion exchange column outlet by AS

The effects of pH and ammonium concentration on removal efficiency of ammonium by air stripping are shown in Fig. 4.

The results obtained from regeneration of column by 1M brine solution and AS in pH=11 show that circulation of brine through the ion exchange column could be achieved after 16 h. (Table 2).

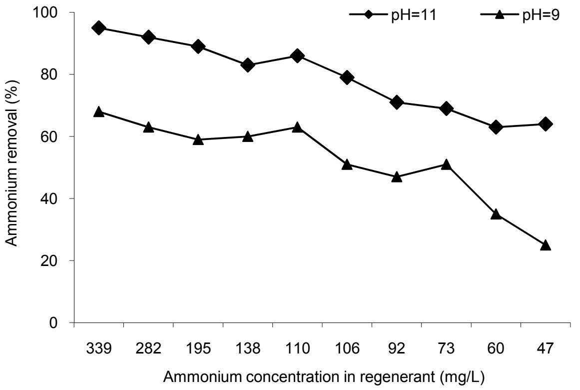

Fig. 4: The effects of pH and ammonium concentration on removal efficiency of ammonium by air stripping

Table 2: Results of brine regeneration test by AS (pH=11)

Test No.	Circulated brine volume (L)	Mesh 20		Mesh 30	
		NH_4^+ conc. in IE effluent (mg/L)	NH_4^+ conc. in regeneration solution (mg/L)	NH_4^+ conc. in IE effluent (mg/L)	NH_4^+ conc. in regeneration solution (mg/L)
1	1	283	0.2	339	0.2
2	7.2	152	69	195	132
3	14.4	80	68	96	115
4	21.6	67	68	63	103
5	28.8	62	57	48	85
6	36	52	45	19	52
7	43.2	41	42	13	37
8	50.4	12	37	11	21
9	57.6	16	25	8	17
NH_4^+ conc. in acid		1645 mg/L		2412 mg/L	

DISCUSSION

In this research, the cation exchange capacity of the Semnan clinoptilolite for ammonium was determined. The obtained results on conditioned zeolite showed that the cation exchange capacity was 9.61 mg NH_4^+/g to 10.06 mg NH_4^+/g (in breakthrough point) and 17.31 mg NH_4^+/g to 18.38 mg NH_4^+/g zeolite as total capacity.

The zeolite particles with mesh 30 had a higher ammonium adsorption capacity than the one with mesh 20. This indicates that the smaller particle size has a higher ion-exchange capacity due to greater available surface areas (Nguyen and Tanner, 1998). The adsorption capacities calculated by graphical integration of the area above the breakthrough curves were about 0.96 and 1.02 meq/g NH_4^+ for particle sizes ranging between 0.42 to 0.84 mm (mesh 30 and 20), respectively. The results are in consistent with the results from previous study (Rahmani *et al.*, 2004). Kazemian has shown that cation exchange capacity of Semnan, Mianeh and Firozkouh zeolite saturated with 1N ammonium were 1.57, 1.5 and 1.76 meq/g, respectively (Kazemian, 1993). In another study, Wang showed that cation exchange capacity of two Chinese natural clinoptilolite were 10.49 and 19.29 mg NH_4^+/g, respectively (Wang *et. al*., 2007).

The results obtained from investigation of factors affecting AS, showed that the ammonium removal effeciency is directly related to pH and ammonium concentration. The best effeciency at pH=9 and 11 were acheived as 68% and 95%, respectively (see Fig. 4). Cotman has shown a 84% removal of ammonium ions by air stripping at pH=11 (Cotman *et al.*, 2004). Therefore in regeneration studies, the solution pH must be controled at 11.

Three loadings and three regeneration cycles were carried out without loss of NH_4^+ adsorption capacity. This shows that on regeneration of the zeolite column with NaCl solution, the Na ions have activated the zeolite column. After the 2nd and 3rd regenerations, the loading process was repeated and it was found that the ammonium adsorption capacity of the clinoptilolite remained constant. This indicates that using NaCl solution, the regeneration of the column could be done repeatedly without loss of ammonium adsorption capacity.

The results from regeneration of ion exchange column outlet by AS showed that reduction of ammonium concentration causes reduction in removal efficiency. According to Corbitt, removal efficiency was low when ammonium concentration was lower than 10 mg/L (Corbitt, 1999). The results showed that total capacity of zeolite in mesh 20 and 30 were 17mg and 18 mg ammonium per gram of the zeolite, respectively. The presence of ammonium in the column were 4327 mg and 4595 mg based on 250 gram of zeolite, respectively. The results showed that the concentration of ammonium was 283 mg/L and 339 mg/L at the regeneration stage and reached to 16 mg/L and 8 mg/L after 16 hours. Therefore, air stripping could remove 87% and 92% of ammonium (equel to 3500 mg and 4140 mg ammonium). The comparison analysis of the results showed that regeneration effeciency of

zeolite with mesh 30 in 12 hours was equal to the effeciency of zeolite mesh 20 in 16 hours. However, ammonia determination in acidic environment showed 1645 mg and 2412 mg of absorption. The absorption efficiency in that concentrations were 47% and 58%, respectively.
In this process, regenerated solution was continuously circulated between IE and AS. Effluent circulation from AS to IE reactor caused the use of existed sodium cations to exchange with ammonia ions, as well as to reach the high level of pH in regeneration solution to change ammonium to ammonia. This method consumes less chemicals as well as lower level of discharge flow. The results demonstrated that absorption effeiciency of amonia is low and ammonia can be emitted to the environment and may cause air pollution. Although incineration of polluted air is one of the control processes, but it can increase operational costs.
Results of the experimental investigation may be used to develop optimum operational conditions for clinoptilolite exchangers. At present, the most wastewater treatment plants in Iran are only designed for removal of organic matters and ammonium remains in the effluent. The use of ion exchange with clinoptilolite and air stripping for regeneration, can lead to economical removal of NH_4^+ from the effluent. It could be concluded that the method studied may be considered as an advanced and applicable process for treating effluents from sources such as closed fishponds in existing treatment plants.

ACKNOWLEDGEMENTS
Authors gratefully acknowledge the financial support of this project by the Department of Environmental Health Engineering, Faculty of Public Health and Center for Health Research, Hamadan University of Medical Sciences.

REFERENCES
APHA, AWWA, WEF, (1998). Standard Methods for the Examination of Water and Wastewater. (19th adn.), Washington DC, APHA.

Celik, M.S., Ozdemir, B., Turan, M., Koyuncu, I., Atesok, G., Sarikaya, H.Z., (2001). Removal of ammonia by natural clay minerals using fixed and fluidized bed column reactors. J. Water Sci. Tec., **1**(1): 81-88.

Corbitt, R.A., (1999). Standard handbook of environmental engineering. New York, McGraw-Hill.

Cotman, M., Zagorc-Koncan, J., (2004). Zgajnar-Gotvajn, A., The relationship bettween composition and toxicity of tannery wastewater. Water Sci Technol, **49**(1): 39-46.

Demir, A., Gunay, A., Debik, E., (2002). Ammonium removal from aqueous solution by ion exchange using packed bed natural zeolite. Water SA Journal, **28**(3): 329-335.

Du, Q., Liu, S., Cao, Z., Wang, Y., (2005). Ammonia removal from aqueous solution using natural Chinese clinoptilolite. Separation and purification technology **44**(3): 229-234.

Emadi, H., Nezhad, J. E., Pourbagher, H., (2001). In vitro Comparison of zeolite (Clinoptilolite) and Activated Carbon as Ammonia Absorbents in Fish Culture. Naga, The ICLARM Quarterly, **24**(1-2): 18-20.

Ershov, A.V., (1984). Use of transcarpathin clinoptilotie rock to remove Ammonium nitrogen from municipal sewage. Khim Tekhnol- Vody **6**: 71-75.

Farkas, A., Rozic, M., Barbaric-Mikocevic, Z., (2005). Ammonium exchange in leakage waters of waste dumps using natural zeolite from the Krapina region, Croatia. J Hazard Mater **117**(1): 25-33.

Haralambous, A., Maliou, E., Malamis, M., (1992). The use of zeolite for Ammonium uptake. Water Sci. Tec. **25**(1): 139-145.

Hargreaves, J. A., Tucker, C. S., (2004). Managing Ammonia in Fish Ponds, SRAC.

Kazemian, H., (1993). Chemical analysis, characterization, and determination of Ion-Exchange properties of Iranian natural zeolites. Chemistry. Isfahan, Iran, University of Isfahan. **M.Sc**.

Lahav, O., Green, M., (1998). Ammonium removal using ion exchange and biological regeneration. Wat. Res **32**(7): 2019-2028.

Nguyen, M. L., Tanner, C.C., (1998). Ammonium removal from wastewaters using natural New Zealand zeolites. New Zealand Journal of Agricultural Research **41**: 427-446.

Rahmani, A. R., Mahvi, A. H., (2006). Use of ion exchange for removal of ammonium: a biological regeneration of zeolite. Global Nest, **8**(2): 146-151.

Rahmani, A. R., Mahvi, A. H., Mesdaghinia, A. R., (2004). Investigation of Ammonium removal from polluted water by Clinoptilolite zeolite. International Journal of Environmental Sci. Tec. **1**(2): 131-141.

Roberts, E., Alley, P. E., (2000). Water quality control handbook, McGraw-Hill.

Semmens, M.J., Porter, P. S., (1979). Ammonium removal by ion exchange: using biologically restored regenerant. J. WPCF **51**(12): 2928-2940.

Tchobanoglouss, G., Burton, F.L., Stensel, H. D., (2003). Wastewater Engineering. New York, McGraw-Hill.

Wang, Y. F., Lin, F., Pang, W.Q., (2007). Ammonium exchange in aqueous solution using Chinese natural clinoptilolite and modified zeolite. J Hazard Mater **142**(1-2): 160-4.