

Ammonium removal from sanitary landfill leachate using natural Gördes clinoptilolite

Dogan Karadag^{a,*}, Sema Tok^a, Eda Akgul^a, Mustafa Turan^b,
Mustafa Ozturk^a, Ahmet Demir^a

^a *Yildiz Technical University, Civil Engineering Faculty, Environmental Engineering, Department, 34349 Besiktas, Istanbul, Turkey*

^b *Istanbul Technical University, Civil Engineering Faculty, Environmental Engineering Department, 34469 Maslak, Istanbul, Turkey*

Received 29 January 2007; received in revised form 7 August 2007; accepted 8 August 2007

Available online 12 August 2007

Abstract

Removal of ammonium ion (NH_4^+) from leachate from Odayeri sanitary landfill, located in the European part of Istanbul, was examined using Gördes (Turkish) clinoptilolite. The effects of pH, flow rate, ammonium concentration and competitive cations on the removal efficiency were investigated in both batch and column studies. Thomas model were used to analyze the breakthrough data. Nonlinear least square method was applied for fitting the column data. The competitive effect was observed more effective in lower ammonium concentration and higher cation concentrations. Conditioning and regeneration using NaCl improved removal efficiency of ammonium from leachate.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Leachate; Ammonium; Clinoptilolite; Competitive ions; Thomas model

1. Introduction

Leachate originating from sanitary landfill sites is one of the major environmental problems since discharging of it may cause serious pollutions to groundwater and surface waters. The chemical characteristic of leachate varies significantly as a function of a number of factors such as waste composition, the degradation degree of waste, moisture content, hydrological and climatic conditions [1]. High concentrations of organic compounds, ammonium, heavy metal and inorganic salts are major characteristic of landfill leachate [2–4]. Ammonium concentration in leachate can be found up to several thousand mg/l [5,6].

The release of high levels of ammonium without treatment decreases the performance of biological treatment systems and accelerates eutrophication, dissolved oxygen depletion and toxicity of living organisms in surface waters [7]. Since hazardous and toxic properties of leachate proceed for a long time period, ammonium removal has become a critical issue of leachate treatment in recent decades.

In order to remove ammonium from leachate, several technologies have been tested, namely biological processes [8], air stripping [9], struvite precipitation [10], adsorption by activated carbon [11] and ion exchange [12]. Among them, ion exchange is a promising method due to its economical advantage, low energy input and easy operation. With its cheaper cost and higher selectivity for ammonium ion, clinoptilolite is a very competitive compared to other adsorbents for ammonium removal.

Our previous study proved that Turkish clinoptilolite is an excellent adsorbent for ammonium removal from synthetic solution with the concentration range of 25–150 mg/l [13]. In this study, batch and column studies were performed for ammonium removal from Odayeri (Istanbul) sanitary landfill leachate using natural clinoptilolite. The parameters namely, pH, flow rate, concentration and competitive ions were evaluated. Breakthrough data were modeled using nonlinear least square method with the help of Microsoft Excel package program.

2. Materials and methods

2.1. Experimental setup

The clinoptilolite was obtained from Esen Company in Gördes region of Turkey and used as an ion exchanger in this

* Corresponding author. Tel.: +90 2122597070; fax: +90 2122619041.
E-mail address: dkaradag@yildiz.edu.tr (D. Karadag).

Table 1
Chemical composition of clinoptilolite

Constituent	Value (wt.%)
SiO ₂	74.4
Al ₂ O ₃	11.5
Fe ₂ O ₃	1.1
K ₂ O	5.0
MgO	0.5
Na ₂ O	0.6
CaO	2.0
TiO ₂	0.1
MnO ₂	<0.001
P ₂ O ₅	0.02
LOI ^a	5.85

^a Loss of ignition.

study. The chemical characteristic of clinoptilolite is given in Table 1. It is mineralogical content is mainly by clinoptilolite (85%) and other components are feldspar (10%) and clay (5%). Cation exchange capacity and bulk density of are 0.95–1.4 meq/g and 900–1100 kg/m³, respectively [13]. Sample was ground and classified to 0.6–1.2 mm. Then it was washed to remove impurities and dried at 103 °C before using in batch experiments. Clinoptilolite was used in column study without any treatments.

Odayeri landfill site is used for the sanitary landfilling of municipal wastes of European side of Istanbul city and it is operated for 10 years. Leachate sample was collected from the landfill basin and characterized just after arrival to laboratory. The sample was stored at 4 °C until usage for experiments. As shown in Table 2, ammonium, sodium and potassium are main cations in the composition of leachate. The leachate was diluted using distilled water in order to obtain several levels of ammonium concentration. The batch experiments were carried out by shaking a 4 g of clinoptilolite with 100 ml leachate solution at 200 rpm.

In order to determine effect of competitive ions on the removal of ammonium, synthetic NH₄⁺, K⁺, Na⁺, Ca²⁺ and Mg²⁺ stock solutions were prepared using NH₄Cl, KCl, NaCl, MgCl₂ and CaOH chemicals. All chemicals used were analytical grade.

Column experiments were conducted using a plexiglas column of 5 cm internal diameter and 60 cm height. The leachate was fed through clinoptilolite bed using peristaltic pump in down-flow mode. Breakthrough curves were obtained as a function of the flow rate (6.8, 11 and 21 ml/min), ammonium

Table 2
Composition of leachate used in experiments

Parameter	Value
pH ^a	8
COD	22,300
Surfactant	0.4
NH ₄ ⁺	3750
Na ⁺	3328
K ⁺	1785
Mg ²⁺	220
Ca ²⁺	36

^a All values are in mg/l except pH.

concentration (100, 200 and 400 mg/l) and pH (6.5, 7.5 and 8.3). When the column exhausted ($C_t/C_o = 1$), the clinoptilolite bed was regenerated using NaCl solution having the pH value of 11. The regeneration solution consisted of 10 and 20 g/l NaCl and was pumped in up-flow mode.

During the all experimental study, the temperature was kept as 25 ± 2 °C and pH of solution was adjusted using NaOH or H₂SO₄ chemicals and Jenway pH meter. Effluent samples were taken at every 30 min and 4 h in batch and column studies, respectively. Ammonium concentration remained in effluent solution was determined using Jenway ammonia selective electrode in conjunction with a digital pH/mV meter. Jenway flame spectrophotometer and Unicam atomic absorption spectrophotometer were used to determine the concentration of K⁺, Na⁺ Ca²⁺ and Mg²⁺ ions, respectively.

2.2. Data modeling

The Thomas model is widely used for modeling the breakthrough data obtained from column studies. Thomas equation is expressed as:

$$C_t = \frac{C_o}{1 + \exp(kQ_oM/v - kC_o t)} \quad (1)$$

Where k is the Thomas model constant (l/mg h), Q_o is the maximum value of ammonium uptaked (mg/g), M is amount of clinoptilolite in column reactor (g), C_o is the influent concentration (mg/l), C_t is the effluent ammonium concentration at time t (mg/l), v is flow rate (l/min) and t is flow time (h).

Nonlinear least square method was preferred for the modeling of batch and column data since it is reported that having better performance than linear analysis [14–15]. Microsoft Excel package program was used for nonlinear analysis and coefficient of determination (R^2) was also used to determine the fitting degree of model outputs with the experimental data. Coefficient of determination is given as:

$$R^2 = \frac{\sum (D_{\text{mod.}} - Da_{\text{exp.}})^2}{\sum (D_{\text{mod.}} - Da_{\text{exp.}})^2 + (D_{\text{mod.}} - D_{\text{exp.}})^2} \quad (2)$$

Where $D_{\text{exp.}}$ is experimental data, $Da_{\text{exp.}}$ is the average value of experimental data and $D_{\text{mod.}}$ is the model output.

3. Results and discussion

3.1. Batch equilibrium

pH is one of the most important parameters controlling the ion exchange process. In order to determine the effect of pH on ammonium removal, experiments were carried out using various pH levels of leachate in the range of 4–10. As shown in Fig. 1, pH has little effect on ammonium removal in the range of 6–8 and the highest value was obtained at pH 7 as 57.8%. These results are well agreement with the data of our previous study [14]. For the pH value of above 8 and below 6, ammonium removal was decreased sharply. At higher pH values, ammonium ions are neutralized by hydroxyl ion rendering it uncharged. Lower

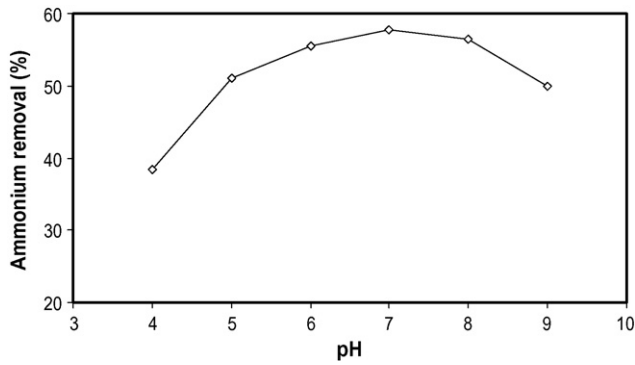


Fig. 1. Effect of pH on the ammonium removal by clinoptilolite ($T=25\text{ }^{\circ}\text{C}$; ammonium concentration = 353 mg/l; stirring time = 1 h).

values of ammonium removal below pH 6 are due to competition of H^+ and NH_4^+ ions for the exchange sites in the clinoptilolite surfaces [16].

As can be seen from Fig. 2, stirring time and concentration has an important role on the ammonium removal capacity of clinoptilolite. Increasing of both stirring time and ammonium concentration promoted amount of ammonium uptake. The equilibrium was reached at 3 h and highest value of ammonium exchanged was 20.37 mg/g for the concentration of 3750 mg/l.

3.2. Effect of competitive cations

Landfill leachate contains large amounts of other cations namely K^+ , Ca^{2+} , Mg^{2+} and Na^+ and these cations can have effects on the removal of ammonium ion. In order to investigate the effect of these cations on ammonium removal, experiments were performed using synthetic ammonium and cationic solutions. For this purpose, concentrations of cations and ammonium in synthetic solution were adjusted between 100 and 1000 mg/l.

The competitive ions affect the equilibrium time and ammonium exchange capacity of clinoptilolite, considerably. As shown in Fig. 3., the equilibrium time was obtained as 40 min (0.67 h) for synthetic solution containing only ammonium and it was increased up to 2 h in the presence of competitive ions. Also the equilibrium time was occurred in 3 h for leachate solution as shown in Fig. 2. These data clearly shows that competitive

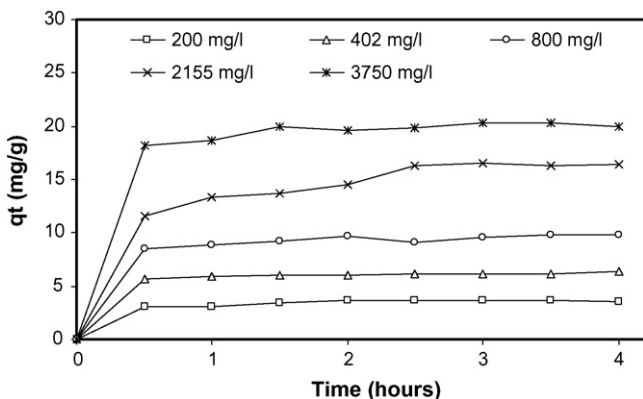


Fig. 2. Kinetics of ammonium removal from leachate using clinoptilolite ($T=25\text{ }^{\circ}\text{C}$; pH 7).

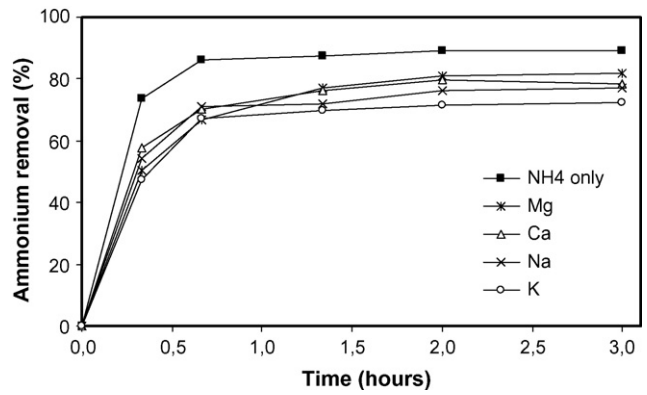


Fig. 3. Effect of competitive ions on the ammonium removal ($T=25\text{ }^{\circ}\text{C}$; pH 7; concentration of cations = 250 mg/l).

ions lowered the uptake of ammonium ions and raised the equilibrium time. Wang et al. (2006) observed similar results for the removal of ammonium from leachate [17].

During the experimental studies maximum ammonium removal was observed in the absence of competitive cations. Comparing of four cations showed that in lower stirring time all cations had similar effects and in equilibrium the competitive degree of cations is listed as K^+ , Na^+ , Ca^{2+} and Mg^{2+} , respectively. Mc Veigh [18] sorted the effect of three cations on ammonium removal as $\text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$. The effect of concentration of competitive cations was investigated for only Na and K ions since they have higher effects on ammonium removal. As shown in Fig. 4, competitive effect was more

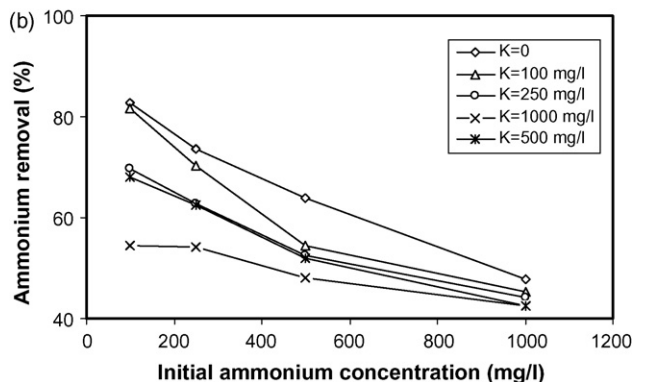
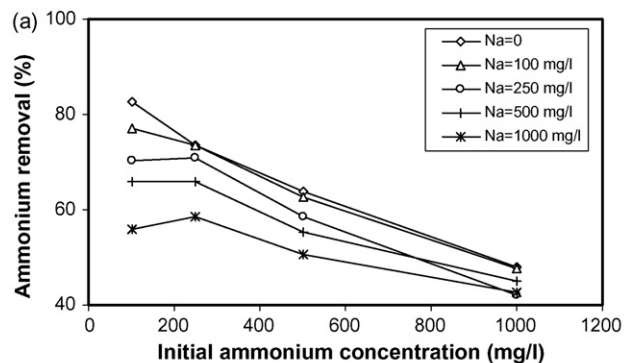


Fig. 4. Effect of sodium (a) and potassium (b) concentration on the removal of ammonium efficiency.

Table 3
The Thomas model constants of column studies

	k (10^{-3}) (ml/min mg)	Q_o (mg/g)	R^2
pH (flow rate: 6.8 ml/min; NH_4 :200 mg/l; bed height: 40 cm)			
6.5	4.45	10.63	0.979
7.5	2.51	16.32	0.965
8.3	3.39	12.70	0.976
Flow rate (NH_4 : 200 mg/l; bed height: 40 cm; pH:7.5)			
6.8 ml/min	2.51	16.32	0.965
11 ml/min	9.25	10.02	0.987
21 ml/min	14.18	8.81	0.997
Concentration (flow rate: 6.8 ml/min; bed height: 40 cm; pH: 7.5)			
100 mg/l	3.83	9.89	0.960
200 mg/l	2.51	16.32	0.965
400 mg/l	3.99	8.74	0.953
Bed height (flow rate: 6.8 ml/min; pH: 7.5; NH_4 :400 mg/l)			
40 cm	3.99	8.74	0.953
60 cm	4.27	9.18	0.959
Regeneration (flow rate: 6.8 ml/min; pH: 7.5; NH_4 : 400 mg/l; bed height: 60 cm)			
Regeneration 1	6.50	9.93	0.992
Regeneration 2	7.87	9.15	0.982
Regeneration 3	9.91	10.92	0.996
Regeneration 4	15.62	9.89	0.963
Regeneration 5	16.97	8.13	0.960

effective in lower ammonium concentration and higher cation concentration.

3.3. Column studies

In column studies the parameters namely pH, flow rate, ammonium concentration and bed height were evaluated for their effect on the ammonium removal. Thomas model was applied for modeling of the column data and the results are summarized in Table 3.

Examination of breakthrough curves exhibits that all run has similar pattern. While the breakthrough point ($C/C_o = 0.1$) was achieved in the first 25% of service time, the rate of ammonium exchange decreased up to about 85% and the higher uptake was occurred in the last 15% of operational time.

As in batch experiments, maximum ammonium removal was achieved in the pH range of 6–8, pH studies in column studies were performed at pH 6.5, 7.5 and 8.3 (natural pH) in order to determine the optimum pH value for practical purposes. The breakthrough curves were constructed against time for three pH values and shown in Fig. 5. It is seen from the figure, the pH 7.5 has better performance than the other pH values. While the breakthrough times were occurred at the time of 65, 44 and 42 running hours for the pH values of 7.5, 8.3 and 6.5, respectively, the time required to reach saturation was 260, 164 and 148 h. The values of Thomas model constants (q_o and k) have similar pattern with the results in Fig. 5. The highest q_o and the lowest k values were obtained for the pH 7.5. Maximum ammonium exchange capacity (q_o) was 16.32 mg/g for pH 7.5 and the lowest value was obtained as 10.63 mg/g for pH 6.5.

Flow rate is one of the important parameters for ion exchange system. Columns were run at different flow rates as 6.8, 11

and 21 ml/min, respectively. The effect of flow rate on the performance of column system is presented in the form of breakthrough curves as in Fig. 6. The C/C_o value remained below 0.1 up to 7, 30 and 65 h for the flow rate of 21, 11 and 6.8 ml/min respectively. The higher saturation time was achieved in the case of lower flow rate. This was due to being driven of ammonium ions through the column before the complete exchange by clinoptilolite at higher flow rates. The results in Table 3 indicate that q_o increased and k decreased with the decreasing of flow rate. Similar results were observed for the metal exchange in fixed bed of zeolite [19].

As seen from Fig. 7, increasing of ammonium concentration decreased the both breakthrough and saturation times of column reactor. Increasing of concentration from 100 to 200 mg/l decreased slightly the performance of ammonium removal, while the breakthrough time was occurred at 72 and 65 h, the

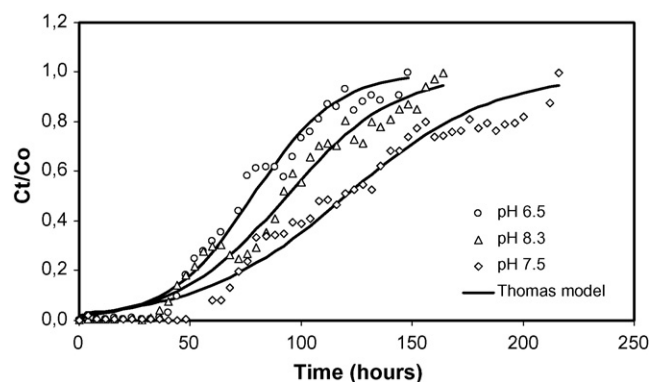


Fig. 5. Breakthrough curves for different pH values (NH_4 : 200 mg/l; flow rate: 6.8 ml/min; bed height: 40 cm).

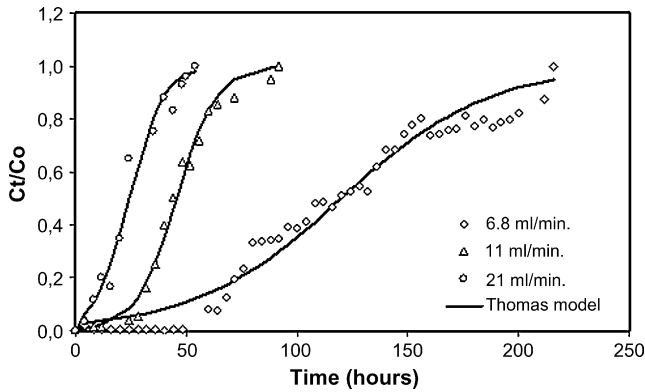


Fig. 6. Breakthrough curves for different flow rates (pH: 7.5; bed height: 40 cm; NH_4 :200 mg/l).

saturation was completed at 260 and 216 h for 100 and 200 mg/l, respectively. Increasing of concentration up to 400 mg/l affected the ammonium removal pattern significantly. The saturation of clinoptilolite bed ($C = C_0$) occurred at the time of 88 h which is slightly higher than the value of breakthrough point of 100 mg/l. The reason for sharp decreasing of column performance at 400 mg/l can be explained by the increasing of ammonium concentration. Also lower diluting rate of leachate to obtain higher ammonium concentration caused to be increased of Na^+ and K^+ concentrations and higher competitive ions decreased the ammonium exchange efficiency. As ammonium concentration increased from 100 to 200 mg/l, ammonium exchange capacity of clinoptilolite also increased up to 16.32 mg/g but decreased to 8.74 mg/g for 400 mg/l. In literature, ammonium capacity increased with increasing of concentration but it decreased in this study which is caused mainly by increasing of competitive ions. The ammonium exchange capacity of 200 mg/l was determined as 3.65 mg/g (0.21 meq/g) in batch study and it increased up to 16.32 (0.91 meq/g) mg/g in column study. Similar results for adsorption experiments were obtained in the literature [20].

In order to investigate the amount of clinoptilolite on the treatment process, the height of bed in column reactor was increased 50%, and the ammonia concentration and flow rate were kept constant as 400 mg/l and 6.8 ml/min. Increasing of bed height caused increasing the breakthrough time and ammonium exchange capacity from 16 to 20 h and 8.74 to 9.18 mg/g, respec-

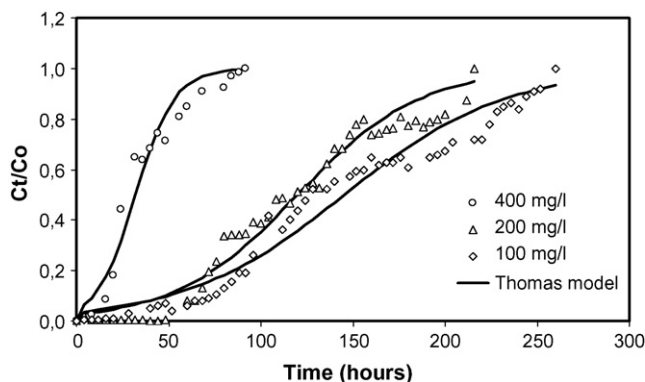


Fig. 7. Comparison of breakthrough curves for different ammonium concentrations (pH: 7.5; bed height: 40 cm; flow rate: 6.8 ml/min).

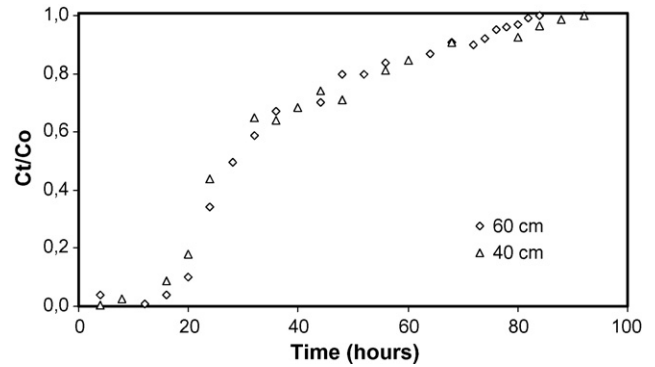


Fig. 8. Effect of bed height on the performance of column reactor (pH: 7.5; NH_4 : 400 mg/l; flow rate: 6.8 ml/min).

tively (Fig. 8). Although the amount of clinoptilolite in column was increased 50%, the breakthrough and ammonium exchange capacities raised as 25% and 5%. The lower increment of treatment efficiency for bed height of 60 cm was attributed to the channeling. Raising the flow rate by 50% in order to provide the contact time equally with bed height of 40 cm caused the increasing the channeling, thus lowering the amount of clinoptilolite contact with leachate.

3.4. Conditioning

The natural clinoptilolite was converted into sodium form by conditioning with NaCl solution in up-flow mode. The performance of natural and conditioned clinoptilolite was compared using breakthrough and saturation capacity in Fig. 9. At a C_t/C_0 value of 0.1 (ammonia removal of 90%), the operating time was 20 and 28 h for natural and preconditioned clinoptilolite. The breakthrough capacity increased by 40% when compared with the capacity obtained using natural clinoptilolite. Although saturation time was reduced from 84 to 46 h after preconditioning, ammonium exchange capacity was increased from 9.18 to 9.86 mg/g. The decreasing of exhausting time and increasing of slope of breakthrough curves is due to removal of cations such as K, Mg and Ca from the structure of the clinoptilolite and locating of sodium ion which is more easily removable from the others. Consequently, preconditioning was found more effective

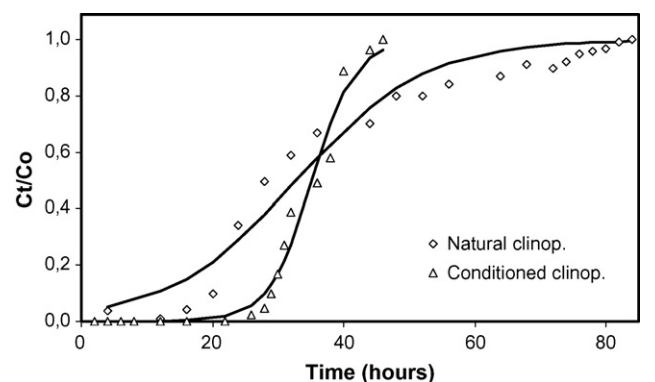


Fig. 9. Comparing the natural and conditioned clinoptilolite (pH: 7.5; NH_4 : 400 mg/l; flow rate: 6.8 ml/min; bed height: 60 cm).

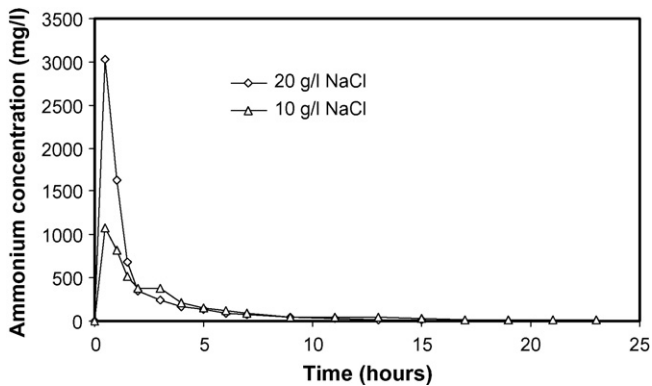


Fig. 10. Regeneration of ammonia from clinoptilolite in column.

than increasing the bed height for the improvement of column performance.

3.5. Regeneration

Clinoptilolite column saturated with ammonium ions was regenerated with the regenerant solution containing 10 and 20 g/l NaCl and a pH of 11 adjusted using NaOH. The results are shown in Fig. 10. The regeneration curves indicate that the displacement of NH_4^+ with Na^+ ions occurred rapidly within 30 min of contact time. The rates of ammonium desorption are much higher at the beginning and lower at the end of the regeneration.

The ammonia concentration in the effluent increased up to 3035 and 1081 mg/l, and regeneration was completed at 15 and 23 h for 20 g NaCl/l and 10 g NaCl/l, respectively. Regeneration with higher NaCl solution enhanced the transformation of exchangeable ions from NH_4^+ to Na^+ and lowered the operation time about 35%. This indicated that a higher NaCl concentration could achieve more complete regeneration than a lower concentration given the same regeneration time period.

Further studies were conducted to investigate the feasibility of regeneration of the clinoptilolite column to see if the column life could be extended. Fig. 11 presents the ammonia breakthrough curves of the clinoptilolite column for each loading after the regeneration cycles. There was an increase in treatment efficiency of column that had been in operation and regenerated five times, compared to natural clinoptilolite. The breakthrough time

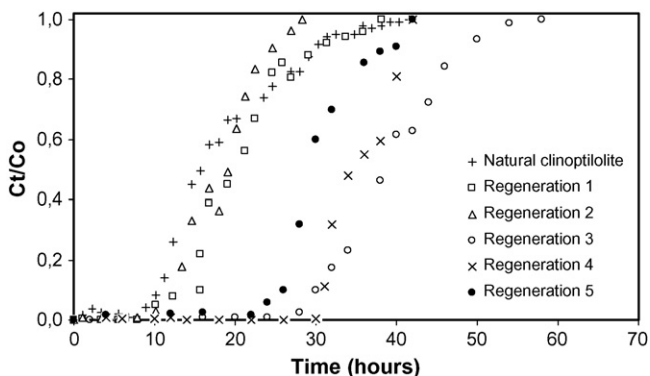


Fig. 11. Comparison of breakthrough curves for natural and regenerated clinoptilolite (pH: 7.5; NH_4 : 400 mg/l; flow rate: 6.8 ml/min; bed height: 60 cm).

was increased from 20 h of natural clinoptilolite to 24, 22, 30 and 31 h at the end of the fourth regeneration and it decreased to 26 h in the fifth cycle. In addition, it is observed that the ammonium exchange capacity was increased from 9.18 to 10.92 mg/g for the operation after the third regeneration. These figures indicate that regeneration improved operation capacity of clinoptilolite column more than 50% and ammonium exchange capacity by 19%. The increasing of treatment efficiency was due to the replacement of calcium, potassium and magnesium exchangeable ions from natural clinoptilolite structure by sodium ions during regeneration. Turan et al. (2005) states that the regeneration expands the size of micropores and enables the increasing the number of ammonium ions accessing more ion exchange sites within the clinoptilolite [21].

4. Conclusions

In this study, effect of some parameters on ammonium removal from leachate onto clinoptilolite was evaluated. Experiments were performed in batch and column mode. Nonlinear least square analysis method was applied to modeling experimental data. In batch experiments, the greater ammonium removal rate was obtained at higher concentration and neutral pH. Inhibition effects of competitive cations were lower at higher ammonium concentration and longer stirring times. Competitive ions increased equilibrium time and lowered ammonium exchange capacity. The sequence of effect of competitive cations was found as potassium, sodium, calcium and magnesium, respectively. Column experiments were performed in order to obtain best conditions for practical purposes. Ammonium removal rate was higher at pH of 7.5, lower flow rate and lower concentration. Ammonium capacity obtained in column was higher than batch system.

Conditioning was improved amount of ammonium exchanged and it was found more effective than increasing the bed height for the improvement of column performance. Regeneration of exhausted clinoptilolite using NaCl increased operation time of column and ammonium exchange capacity

References

- [1] F. Wang, D.W. Smith, G.M. El-Din, Application of advanced oxidation methods for landfill leachate treatment—a review, *J. Environ. Eng. Sci.* 2 (2003) 413–427.
- [2] T.H. Christensen, P. Kjeldsen, P.L. Bjerg, D.L. Jensen, J.B. Christensen, A. Baum, H. Albrechtsen, G. Heron, Biogeochemistry of landfill leachate plumes, *Appl. Geochem.* 16 (2001) 659–718.
- [3] D. Trebouet, J.P. Schlumpf, P. Jaouen, F. Quemeneur, Stabilized landfill leachate treatment by combined physicochemical–nanofiltration processes, *Water Res.* 35 (12) (2001) 2935–2942.
- [4] F. Kargi, M.Y. Pamukoglu, Simultaneous adsorption and biological treatment of pre-treated landfill leachate by fed-batch operation, *Process Biochem.* 38 (2003) 1413–1420.
- [5] X.Z. Li, Q.L. Zhao, X.D. Hao, Ammonium removal from landfill leachate by chemical precipitation, *Waste Manage.* 19 (1999) 409–415.
- [6] B. Wichitsathian, S. Sindhuja, C. Visvanathan, K. Ahn, Landfill leachate treatment by yeast and bacteria based membrane bioreactors., *J. Environ. Sci. Health Part A—Toxic/Hazard. Substances Environ. Eng.* A39 (9) (2004) 2391–2404.

- [7] J.H. Bae, S.K. Kim, H.S. Chang, Treatment of landfill leachates: ammonia removal via nitrification and denitrification and further COD reduction via fenton's treatment followed by activated sludge, *Water Sci. Technol.* 36 (12) (1997) 341–348.
- [8] U. Welander, T. Henrysson, T. Welander, Biological nitrogen removal from municipal landfill leachate in a pilot scale suspended carrier biofilm process, *Water Res.* 32 (5) (1998) 1564–1570.
- [9] K.C. Cheung, L.M. Chu, M.H. Wong, Ammonia stripping as a pretreatment for landfill leachate, *Water, Air Soil Pollut.* 94 (1-2) (1997) 209–221.
- [10] I. Ozturk, M. Altinbas, I. Koyuncu, O. Arıkan, C.G. Yangin, Advanced physico-chemical treatment experiences on young municipal landfill leachates, *Waste Manage.* 23 (2003) 441–446.
- [11] A.A. Hamidi, N.A. Mohd, S. Mohd, A. Salina, Removal of ammoniacal nitrogen (N-NH₃) from municipal solid waste leachate by using activated carbon and limestone, *Waste Manage. Res.* 22 (2004) 371–375.
- [12] A. Papadopoulos, E.G. Kapetanios, M. Loizidou, Studies on the use of clinoptilolite for ammonia removal from leachates, *J. Environ. Sci. Health A31* (1) (1996) 211–220.
- [13] D. Karadag, Y. Koc, M. Turan, B. Armagan, Removal of ammonium ion from aqueous solution using natural Turkish clinoptilolite, *J. Hazard. Mater.* B136 (2006) 604–609.
- [14] D. Karadag, Y. Koc, M. Turan, M. Ozturk, A comparative study of linear and non-linear regression analysis for ammonium exchange by clinoptilolite zeolite, *J. Hazard. Mater.* 144 (1–2) (2007) 432–437.
- [15] R. Han, Y. Wang, W. Zou, Y. Wang, Jie Shi, Comparison of linear and non-linear analysis in estimating the Thomas model parameters for methylene blue adsorption onto natural zeolite in fixed-bed column, *J. Hazard. Mater.* 145 (1–2) (2007) 331–335.
- [16] N.P. Hankins, S. Pliankarom, N. Hilal, An equilibrium ion-exchange study on the removal of NH₄ ion from aqueous effluent using clinoptilolite, *Sep. Sci. Technol.* 39 (15) (2004) 3639.
- [17] Y. Wang, S. Liu, Z. Xu, T. Han, S. Chuan, T. Zhu, Ammonia removal from leachate solution using natural Chinese clinoptilolite, *J. Hazard. Mater.* 136 (2006) 735–740.
- [18] R. J. Mc Veigh, The enhancement of ammonium ion removal onto columns of clinoptilolite in the presence of nitrifying bacteria, Ph.D. Research Dissertation, Department of Chemical and Process Engineering, The Queen's University of Belfast, 1999.
- [19] R. Hana, W. Zoub, H. Li, Y. Li, J. Shi, Copper(II) and lead(II) removal from aqueous solution in fixed-bed columns by manganese oxide coated zeolite, *J. Hazard. Mater.* B137 (2006) 934.
- [20] M. Sprynskyy, M. Lebedynets, R. Zbytniewski, J. Namiesnik, B. Buszewski, Ammonium removal from aqueous solution by natural zeolite, Transcarpathian mordenite, kinetics, equilibrium and column tests, *Sep. Purif. Technol.* 46 (3) (2005) 155–160.
- [21] M. Turan, H. Gulsen, M.S. Celik, Treatment of landfill leachate by a combined anaerobic fluidized bed and zeolite column system., *J. Environ. Eng., ASCE* 131 (2005) 815–819.