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Ammonium Removal from Municipal Landfill Leachate by Clinoptilolite Bed Columns: Breakthrough Modeling and Error Analysis

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In this study, a clinoptilolite bed column system was used to remove ammonium from municipal landfill leachate. Laboratory-scale column experiments were conducted in upflow fixed-bed and fluidized-bed modes with different ammonium concentrations. Ammonium removal was managed mainly by Ca^{2+} and K^+ cations of clinoptilolite, and higher treatment performances were obtained at lower flow rates. On the other hand, higher effluent volumes and removal rates were produced by lower ammonium concentrations, and increased expansion ratios in the fluidized-bed column reduced the treatment efficiency. The sum of normalized errors (SNE) procedure was applied using five different error functions to model the experimental data. The Clark and Yoon−Nelson kinetic models were applied to column data to predict the breakthrough data, and the results indicated that the Clark model is better for modeling the experimental data. Ammonia stripping was investigated as a pretreatment step to obtain lower ammonium concentrations in the effluent. With a 12-h aeration time at pH 12, the ammonium concentration of leachate was decreased from about 3000 to below 400 mg/L. These results indicate that combining ammonia stripping and an upflow fixed-bed system is feasible in reducing higher ammonium concentrations to satisfactory levels.

1. Introduction

Sanitary landfilling is the most common municipal solid waste management practice followed throughout the world. The major problems caused by landfilling are related to the generation of highly contaminated leachates that pose long-term environmental problems. Ammonium is the most significant long-term pollutant of leachate, and its concentration increases up to 4000 mg/L.[1−3] On the other hand, the release of high levels of ammonium into water bodies without proper treatment can have toxic effects on aquatic organisms. Therefore, treatment of high ammonium contents in leachate is of great importance to avoid serious environmental problems.

Among many treatment alternatives, ammonium removal by ion exchange is very attractive when a low-cost exchanger is used. Many researchers have reported that ion exchange with natural zeolite is attractive because of its low cost and relatively simple application.[4−6] Clinoptilolite is a natural aluminosilicate zeolite mineral that contains exchangeable cations, such as Na^+, K^+, Ca^{2+}, and Mg^{2+}, in its structural framework. Ammonium ions in wastewater can replace these cations during the treatment process.[7,8]

Ammonium removal by clinoptilolite can be accomplished in batch or column mode. Batch studies have been widely preferred by researchers to examine the effects on the ammonium removal of parameters such as pH, contact time, ammonium concentration, temperature, and competitive ions.[9−11] Although batch experiments are easily performed in the laboratory, column studies are more suitable for practical applications of continuous pollutant treatment. Our previous study demonstrated that Gördes clinoptilolite is very effective for ammonium removal in downflow column operation.[11] In this study, clinoptilolite column reactors were operated in upflow and fluidized modes for the treatment of ammonium from Odayeri landfill leachate. The Yoon−Nelson and Clark kinetic models were applied to predict the dynamic behavior of breakthrough data. Finally, ammonium stripping was investigated as a pretreatment step because of the insufficiency of ion exchange for the treatment of high ammonia levels.

2. Materials and Methods

2.1. Clinoptilolite and Leachate Sample. The clinoptilolite sample used as an ion exchanger was obtained from the Gordes region of Turkey, and its chemical analysis is provided elsewhere.[11] Its mineralogical content mainly consists of clinoptilolite (85%) with minor components of feldspar (10%) and clay (5%). The cation-exchange capacity and bulk density of the sample were supplied by the producer as 0.95−1.4 mequiv/g and 900−1100 kg/m³, respectively. The sample was ground and sieved to 0.6−1.2 mm before being used in experimental studies.

The landfill leachate used in the experiments was obtained from the Odayeri landfill site and stored at 4 °C in the laboratory. As shown in Table 1, ammonium, sodium, and potassium were the main cations in the leachate. The leachate was diluted using distilled water in order to obtain several ammonium concentration levels.

2.2. Experimental Procedure. Clinoptilolite samples were washed with distilled water to remove impurities and dried in an oven at 103 °C overnight before use in batch studies. Four grams of clinoptilolite was mixed at 200 rpm with 100 mL of leachate solution having an initial ammonium content in the

Table 1. Characteristics of Leachate

parameter	value
pH	7.8–8.3
COD (mg/L)	10874–22300
NH_4^+ (mg/L)	1815–3750
TKN (mg/L)	2020–3870
Na^+ (mg/L)	1364–3328
K^+ (mg/L)	726–1785
Mg^{2+} (mg/L)	135–220
Ca^{2+} (mg/L)	36–234

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range of 194−3750 mg/L. In the fixed- and fluidized-bed studies, the experiments were conducted using a plexiglas column with an inner diameter of 5 cm and a height of 60 cm. The column was filled with the clinoptilolite sample to a level of 40 cm, which corresponded to a weight of 600 g. The leachate was fed through the clinoptilolite bed using a Masterflex100 peristaltic pump. The bed height was increased to 44, 48, and 60 cm by increasing the flow rate to obtain bed expansion ratios of 10%, 20%, and 50%, respectively. All column experiments were conducted at room temperature, and the initial solution pH was adjusted by addition of 1 N H_2SO_4 solution by a Jenway pH meter. Because a previous study showed that maximum ammonium removal was obtained at pH 7.5, all experimental studies were performed at this pH value.[11] Breakthrough curves were established as a function of different flow rates (6.8, 11, and 21 mL min^{-1}), ammonium concentrations (100, 200, and 400 mg/L), and expansion ratios (10%, 20%, and 50%). Effluent samples were taken at every 4 h, and the ammonium concentration was determined using a Jenway ammonia-selective electrode in conjunction with a digital pH/mV meter. A Unicam atomic absorption spectrophometer (Unicam 929 A) was used for measuring the concentrations of K^+, Na^+, Ca^{2+}, and Mg^{2+} ions. All analyses were carried out according to standard methods.[12]

Ammonia stripping experiments were performed in 3-L beakers, and fine bubble diffusers were used for aeration. During the experiments, the effects of pH and aeration time on the removal efficiency of ammonia were investigated. All experimental studies were conducted at room temperature, and 10 M NaOH solution was used for adjusting the pH of the leachate.

2.3. Determination of Equilibrium Parameters in the Column. Breakthrough curves are commonly used to represent the effluent pollutant concentration versus operating time or wastewater volume treated. Bed volume (BV) is a unit commonly used in the column studies and refers to the volume of wastewater treated compared to the volume of the treatment bed[13]

$$BV = \frac{V_F}{V_R} \tag{1}$$

where V_F (mL) is the total water volume passed in the column during ammonium exchange and V_R (mL) is the volume of the clinoptilolite bed in this case.

The ion-exchange capacity of clinoptilolite bed for a given influent ammonium concentration at a given flow rate was determined by the integration of the area above the breakthrough curve and can be calculated by the equation[14]

$$F_M = Q \int_0^t (C_0 - C_t) \, dt \tag{2}$$

where C_0 (mg/L) and C_t (mg/L) are the concentrations of ammonium in the influent and in the effluent at any time t, respectively; Q (mL/L) is the flow rate of leachate, and t is the operating time (h).

Similarly, the total amount of ammonium sent to the column (F_T) is expressed as

$$F_T = QC_0t \tag{3}$$

The quantity of ammonium exchanged per gram of clinoptilolite at any time is defined as

$$q_t = \frac{F_M}{m} \tag{4}$$

where F_M (mg) is the total quantity of ammonium ions exchanged by the clinoptilolite bed at any time and m (g) is the mass of clinoptilolite in the column.

The total ammonium removal percentage is the ratio of the total quantity of ammonium (F_M) to the total amount of ammonium sent to the column (F_T) and is given by the equation

$$R \, (\%) = \frac{F_M}{F_T} \tag{5}$$

2.4. Modeling of the Batch and Column Systems. In this study, five different error functions were used to model the experimental data by minimizing the respective error values using nonlinear regression analysis. Nonlinear regression analysis was performed using Microsoft Excel with the solver add-in program. The error functions studied are given below. In the model equations, d_m is data calculated using the model, d_e is experimental data, s is the number of experimental data points, and p is the number of model parameters.

Sum of the Squares of the Errors (SSE). The SSE function is most frequently used, but it has a major drawback. It provides a better fit as the magnitude of the errors increase, thus biasing the fit toward the high-concentration data

$$SSE = \sum_1^n (d_m - d_e)^2 \tag{6}$$

Sum of Absolute Errors (SAE). This approach is similar to the SSE function

$$SAE = \sum_1^n |d_m - d_e|_i \tag{7}$$

Average Relative Error (ARE).[15] The ARE minimizes the fractional error distribution across the entire concentration range

$$ARE = \frac{100}{s} \sum_1^n \left| \frac{d_m - d_e}{d_e} \right|_i \tag{8}$$

Hybrid Fractional Error Function (HYBRID).[16] This error function was developed to improve the fit of the sum of the squares of the errors (SSE) method at low concentration values. This error function was developed by Porter et al. to improve the fit of the SSE method at low concentration values by dividing by the experimentally measured value. In addition, a divisor is included as a term for the number of degrees of freedom for the system, i.e., the number of data points minus the number of parameters within the isotherm equation

$$HYBRID = \frac{100}{s-p} \sum_{i=1}^n \left[\frac{(d_m - d_e)^2}{d_e} \right]_i \tag{9}$$

Marquardt's Percent Standard Deviation (MPSD).[17] The MPSD is similar to a geometric mean error distribution modified according to the number of degrees of freedom of the system

$$MPSD = 100 \sqrt{\frac{1}{s-p} \sum_{i=1}^n \left(\frac{d_m - d_e}{d_e} \right)_i} \tag{10}$$

As each error function produces different values for model parameters, it is difficult to directly identify an overall optimum parameter set. Thus, the sum of normalized errors (SNE) procedure was employed to provide a better comparison between the parameter values for the different models.

The SNE values were calculated as follows: (1) Each error function was selected in turn, and each parameter set was determined by minimizing the value of the error function. (2)
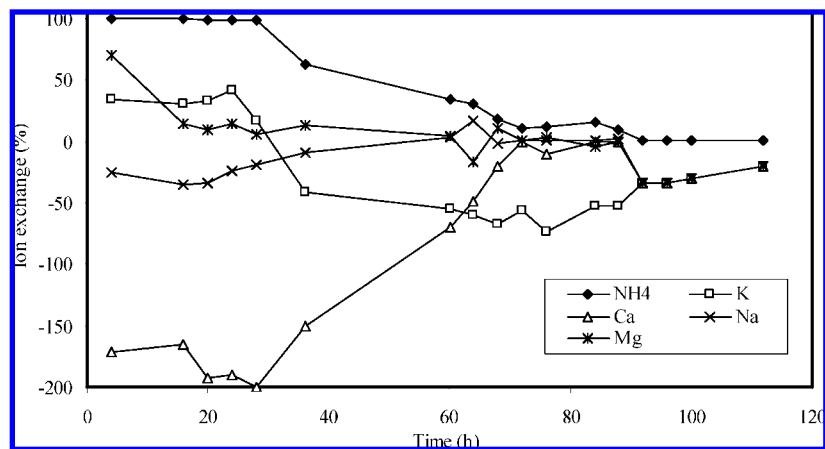
Figure 1. Ammonium-exchange mechanism in a clinoptilolite bed.

The errors determined for a given error function were divided by the maximum error to obtain normalized error values for each parameter set. (3) The normalized errors for each parameter set were summed. (4) The parameter set with the lowest SNE degrees was selected as the best-fit values.

3. Results and Discussion

3.1. Mechanism of Ammonium Removal in the Column. The investigation of the ammonium-exchange mechanism in the clinoptilolite bed was conducted at a concentration of 200 mg L^{-1} and an upflow rate of 6.8 mL min^{-1}, and the results are given in Figure 1. Positive values of the ion-exchange ratio in the figure indicate the ratio of ammonium bound by clinoptilolite, and negative values are ratios of ions released by the clinoptilolite bed.

In early times of operation, sorption of NH_4^+, Mg^{2+}, and K^+ ions occurred throughthe displacement of Ca^{2+} and Na^+ ions in the clinoptilolite structure. However, as the operating time increased, the ion-exchange behavior of Na^+, Mg^{2+}, and K^+ exhibited a sharp change. After the breakthrough point ($C/C_0 = 0.10$), Na^+ and Mg^{2+} ions were not involved in the ion-exchange mechanism, and the sorption of NH_4^+ and desorption of Ca^{2+} sharply decreased. During the experimental studies, the most interesting results were obtained for the exchange of K^+ ion. The breakthrough point shifted the exchange behavior of K^+ from sorption to desorption.

Generally, the pattern of Ca^{2+} desorption from clinoptilolite is similar to the pattern of NH_4^+ sorption in all exchange processes. Taken as a whole, the values in Figure 1 imply that the overall uptake of NH_4^+ is governed mainly by Ca^{2+} and K^+ ions in the cation-exchange sites of the clinoptilolite. Similar results were obtained by for ammonium and metal exchange by clinoptilolite.[18,19]

3.2. Effect of Flow Rate in the Column. In this study, ammonium removal in an upflow clinoptilolite bed was examined at different flow rates and influent ammonium concentrations. The experimental results are presented as breakthrough curves, and evaluations were made using the values of ammonium quantity exchanged per gram of clinoptilolite (q), the ammonium removal efficiency (R), and volume of leachate treated in the column (BV) at the breakthrough and exhaustion points. In the present study, the breakthrough point in the breakthrough curve is referred to 90% removal efficiency ($C/C_0 = 0.10$), and exhaustion point is referred to the point where the effluent concentration reaches the influent concentration ($C/C_0 = 1$).
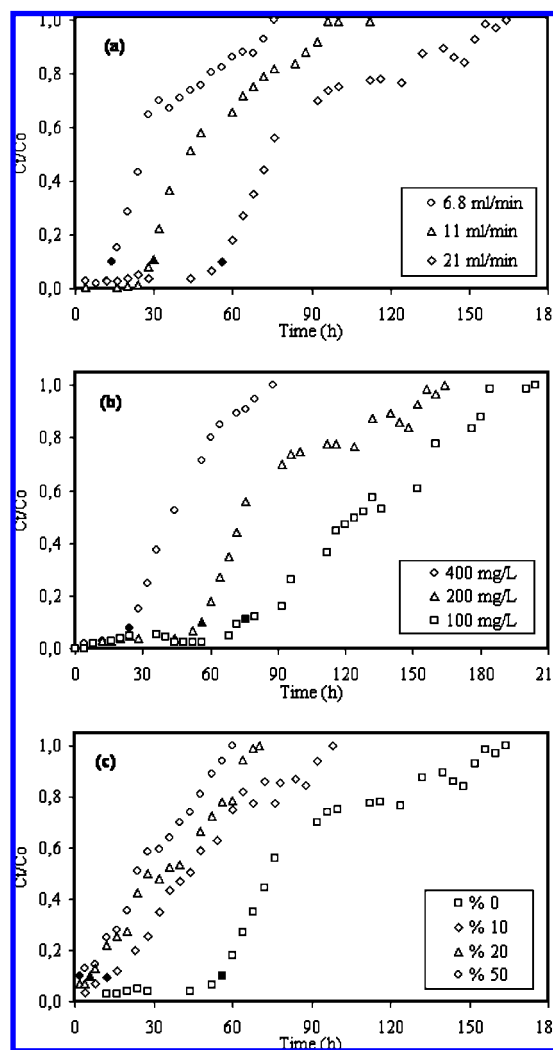

Figure 2. Breakthrough curves under different experimental conditions.

Figure 2a shows the breakthrough curves obtained at different flow rates of leachate with a concentration of 200 mg/L. The breakthrough points occurred at operating times of 56, 30, and 14 h for flow rates of 6.8, 11, and 21 mL/min, respectively. Similarly, the breakthrough capacity of the column decreased from 29.11 to 22.47 BV with the increase in flow rate. As seen from the data in Table 2, the increase in flow rates also led to a decrease in both the amount of ammonium exchanged per gram of clinoptilolite and the total removal efficiency at the

Table 2. Calculated Equilibrium Parameters for Different Experimental Conditions

|	operation time (h)	BV	q (mg g^{-1})	R (%)
flow rate (mL/min)				
6.8	56	29.11	6.78	49.61
11	30	25.10	5.61	42.33
21	14	22.47	4.06	37.71
concentration (mg/L)				
100	76	39.10	4.69	60.12
200	56	29.11	6.78	49.61
400	26	13.05	5.77	47.06
bed expansion ratio (%)				
0	56	29.11	6.78	49.61
10	14	6.24	1.38	42.59
20	6	3.12	0.60	43.64
50	2	1.04	0.30	42.93

exhaustion point. Lower removal efficiency and capacity values were due to the insufficient retention time for complete exchange of ammonium ions in the clinoptilolite bed.

3.3. Effect of Ammonium Concentration in the Column. The breakthrough curves for different initial NH$_4$$^+$ concentrations are displayed in Figure 2b. A comparison of the breakthrough curves shows that, when the initial NH$_4$$^+$ concentration decreased from 400 to 100 mg/L, the time needed to reach the breakthrough and exhaustion points increased. On the other hand, total removal efficiency decreased with increasing ammonium concentration. The maximum ammonium-exchange capacity was obtained as 4.69 mg/g for a concentration of 100 mg/L, and it increased to 5.77 mg/g when the ammonium concentration was increased to 400 mg/L. Sprynskyy et al.[20] used natural zeolite for ammonium removal from a synthetic solution and obtained an ammonium-exchange capacity in the range of 7.30−15.73 mg/g for an ammonium concentration of 100 mg/L. A comparison of these values indicates that competitive ions in the leachate have a negative effect on the ammonium uptake of clinoptilolite.[11]

In the literature, it is reported that the valences of the exchanging cations have a strong effect on ion-exchange equilibrium, and this is referred to as "concentration-valency effect".[21−23] If the exchanging ions are not of equal valence, the equilibrium is a function of the total concentration, and at higher concentrations, it is shifted to favor absorption of the lower-charge cations and, consequently, to exclude more highly charged cations from the clinoptilolite. As shown in section 3.1, removal of ammonium was governed mainly by K$^+$ and Ca^{2+} cations in clinoptilolite, and it is expected that dilution has a positive effect on the column performance.

3.4. Effect of Bed Expansion. The ammonium removal performance of the fluidized bed was also investigated at an ammonium concentration of 200 mg/L. Figure 2c presents a comparison of breakthrough curves obtained with a fixed bed (bed expansion = 0%) and a fluidized bed (bed expansion ratio = 10−50%). At the highest expansion ratio (50%), a volume of only 1.04 BV of leachate was treated, and the amount of ammonium was reduced to 0.30 mg/g at the breakthrough point. Ammonium removal in the fluidized bed decreased sharply with increasing bed expansion ratio. Hovever, the breakthrough capacity of the fluidized bed at the lowest expansion ratio (10%) was lower than that of the fixed bed. Increasing expansion of the bed might have caused an increase in the distance between clinoptilolite particles, thereby allowing ammonium ions to leave the column easily without complete contact with these particles.

3.5. Breakthrough Modeling. Successful design of a column system is primarily based on the proper prediction of the dynamic behavior of adsorption. A description of the adsorption
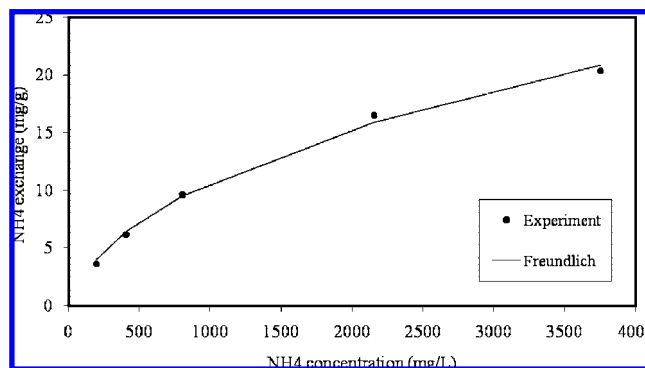
Figure 3. Freundlich modeling of batch experimental data.

Table 3. Calculation of Freundlich Constants with Error Analysis

	SSE	SAE	ARE	HYBRID	MPSD
K_f	0.848	0.848	0.708	0.778	0.762
n	2.494	2.513	2.326	2.421	2.404
SSE	**0.800**	1.113	2.616	0.907	1.018
SAE	1.762	**1.656**	1.938	1.749	1.775
ARE	3.997	3.753	**2.461**	3.059	2.901
HYBRID	2.521	3.034	4.377	**2.024**	2.089
MPSD	7.858	8.257	8.161	6.374	**6.282**
SNE	3.743	3.912	4.604	**3.249**	3.269

process also helps to determine the effluent concentration of adsorbate and to operate the treatment process efficiently. In this study, the Yoon−Nelson and Clark models were used to analyze the breakthrough behavior of the fixed and fluidized beds. The formula of Yoon−Nelson model is given by[24]

$$\frac{C_t}{C_0 - C_t} = \exp(k_{YN}t - \delta k_{YN}) \tag{11}$$

where k_{YN} is a rate constant and δ is the time required for 50% breakthrough capacity.

The Clark model assumes that adsorption follows the Freundlich isotherm model and that the removal rate of pollutant in a column system is determined by the outer mass-transfer step.[25] The equation of the Clark model is given by

$$\frac{C_t}{C_0} = \frac{1}{(1 + Ae^{-rt})^{1/(n-1)}} \tag{12}$$

where A and r are parameters of the Clark model and n is the constant from the Freundlich isotherm model.

To determine the value of n used in the Clark model, batch experimental data were used to estimate the constants of the Freundlich model. The constants were calculated by nonlinear regression analysis using the sum of normalized errors (SNE) procedure. The equation of the Freundlich[26] model is

$$q_e = K_f C_e^{1/n} \tag{13}$$

In this equation, q_e and C_e are the amount of ammonium exchanged by clinoptilolite and the ammonium concentration in solution at equilibrium, respectively. K_f and n are the constants of the Freundlich model.

As shown in Figure 3, the amount of ammonium exchanged increased with increasing initial concentration, and the maximum ion-exchange capacity was obtained as 20.37 mg/g (1.32 mequiv/g). The calculated values of the parameters and error functions are reported in Table 3, and the minimum SNE values for the relevant error functions are indicated in bold type. The SNE data indicate that the HYBRID error function provided the lowest error values with the experimental data. Similarly,

**Table 4. Estimated Column Model Parameters Using Different Error Functions**

	SSE	SAE	ARE	HYBRID	MPSD
			Yoon–Nelson		
k_{YN}	0.0503	0.0472	0.0605	0.0636	0.0549
δ	82.465	85.068	80.000	83.030	90.000
SSE	**0.129**	0.137	0.146	0.161	0.221
SAE	1.487	**1.477**	1.522	1.640	1.771
ARE	30.145	31.503	**25.747**	27.094	24.964
HYBRID	2.459	2.453	1.822	**1.452**	1.793
MPSD	303.781	300.277	242.218	196.086	**176.994**
SNE	4.378	4.438	3.876	**3.752**	4.104
			Clark		
A	197.3	197.3	586.1	1069.3	645.1
r	0.057	0.056	0.065	0.078	0.063
SSE	**0.151**	0.154	0.245	0.196	0.330
SAE	1.676	**1.668**	1.866	1.763	2.042
ARE	42.112	40.588	**23.268**	24.683	24.070
HYBRID	3.113	2.903	1.924	**1.571**	2.404
MPSD	353.064	335.269	171.307	185.129	**165.101**
SNE	4.279	4.131	3.312	**3.071**	3.812

nonlinear modeling studies in the literature indicate that the HYBRID error function generally produces the lowest SNE values.[27,28] The values in Table 3 show that the n and K_f constants were calculated as 2.421 and 0.778, respectively, for ammonium removal from Odayeri landfill leachate.

The estimated values of model parameters and error functions for breakthrough data are presented in Table 4. Again, the minimum SNE values for the relevant error functions are indicated in bold type. According to the values in the table, the HYBRID error function provided the lowest error values with the breakthrough data. The values in the Table 4 indicate that the two kinetic models exhibited somewhat close error values, and the lowest SNE values were found to be 3.752 and 3.071 for the Yoon–Nelson and Clark models, respectively. A comparison of these results shows that the Clark model exhibited a better fit for the column kinetic data.

3.6. Ammonia Stripping. As indicated in section 3.2, the volume of leachate treated and the amount of ammonium exchanged by clinoptilolite decreased sharply with increasing ammonium concentration. These results reveal that individual ion exchange is insufficient to decrease high ammonium concentrations to desirable levels. The subsequent experiments were conducted to investigate ammonia stripping as a pretreatment step prior to ammonia exchange in a fixed column reactor.

Because pH is a major factor affecting the equilibrium of NH_3 and NH_4^+ in the solution, the effect of pH on ammonium removal was studied at different aeration times, and the results are displayed in Figure 4a. During 4 h of aeration, the removal of ammonia increased with increasing pH, and the maximum efficiency was obtained at pH 12. Subsequent experiments were conducted at pH 12 in order to improve the ammonia stripping performance. As with pH, aeration time was found to have a positive effect on the ammonia stripping, and an increasing rate was observed for the first 12 h of aeration time (Figure 4b). After the first 12 h of aeration, an ammonia removal of 88% was achieved, and the ammonia concentration in the leachate solution decreased below 400 mg/L. During the aeration, the rate of ammonia stripping decreased, and 98% of the ammonia was removed from the leachate at the end of 24 h of aeration. These results indicate that ammonia stripping at higher pH is very effective in reducing the ammonia concentration from about 3000 to below 400 mg/L in 12 h of aeration. Similarly, Silva et al.[29] found that ammonia stripping was effective as a post treatment step to reduce ammonium level of sanitary landfill leachate. Ozturk et al.[30] and Calli et al.[31] applied different post-
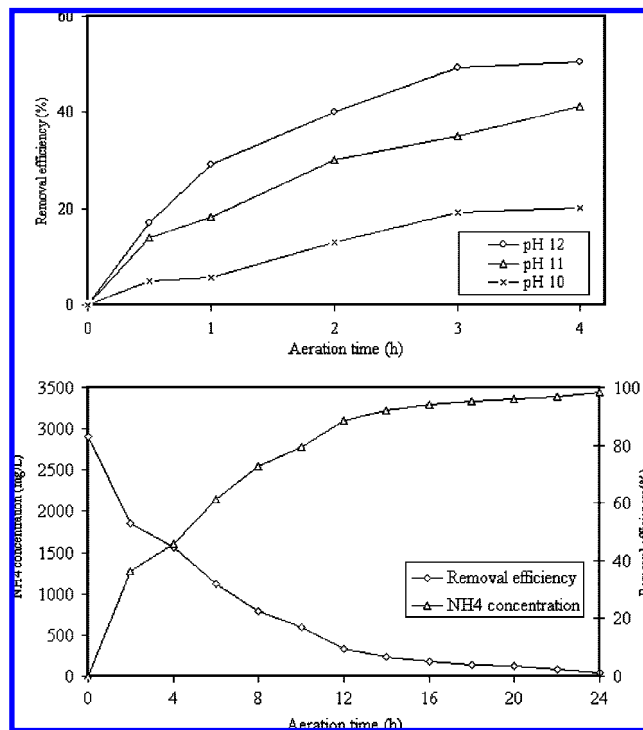
Figure 4. Changes in removal efficiency and ammonia concentration with pH and aeration time.

treatment methods to remove leachate ammonium from Odayeri and Komurcuoda landfill sites in Istanbul, Turkey, and achieved high treatment efficiencies above 90% with ammonia stripping. Ozturk et al.[30] also made an economic evaluation comparing operating costs and concluded that ammonia stripping was a more feasible post-treatment alternative for removal of high ammonia levels from leachate. Consequently, a combination of ammonia stripping and ion exchange in an upflow fixed bed can be used successfully for the treatment of leachate with a high ammonium content.

4. Conclusions

This study was primarily focused on the removal of ammonium from municipal landfill leachate by a clinoptilolite bed column in upflow fixed- and fluidized-bed modes. Experimental studies were conducted at various conditions, and the following conclusions were drawn from this study:

(1) Removal of NH_4^+ is governed mainly by Ca^{2+} and K^+ ions in the cation-exchange sites of clinoptilolite.

(2) Higher treatment efficiencies were obtained at lower flow rates, ammonium concentrations, and bed expansion ratios. The leachate volume treated in the upflow fixed bed at 90% treatment efficiency decreased from 29.11 to 22.47 BV when the flow rate was increased from 6.8 to 21 mL/min. Similarly, increasing the ammonium concentration from 100 to 400 mg/L reduced the volume of leachate treated at the breakthrough point from 39.10 to 13.05 BV.

(3) The fixed bed resulted significantly higher performances than the fluidized bed. Operating the column at a 50% fluidization ratio reduced the effluent volume sharply from 29.11 to 1.04 BV. In the fluidized-bed experiments, higher ammonium removal was achieved with the 10% fluidization ratio.

(4) Modeling studies revealed that the HYBRID function provided the lowest error values and the Yoon–Nelson model exhibited the best fit with the breakthrough data.

(5) Ammonia stripping was investigated as a pretreatment step, and 12 h of aeration at pH 12 decreased the ammonia concentration from about 3000 mg/L to desirable levels. According to these results, it can be concluded that combining air stripping and ammonium exchange with an upflow clinoptilolite bed provides reasonable performance for the treatment of high-ammonia leachate.

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