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The Effect of Modification and Initial Concentration on Ammonia Removal from Leachate by Zeolite

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Abstract**—**The purpose of this study is to investigate the capacity of natural Turkish zeolite for NH_4-N removal from landfill leachate. The effects of modification and initial concentration on the removal of NH_4-N from leachate were also investigated. The kinetics of adsorption of NH_4-N has been discussed using three kinetic models, i.e., the pseudo-second order model, the Elovich equation, the intraparticle diffuion model. Kinetic parameters and correlation coefficients were determined. Equilibrium isotherms for the adsorption of NH_4-N were analyzed by Langmuir, Freundlich and Tempkin isotherm models. Langmuir isotherm model was found to best represent the data for NH_4-N.

Keywords**—**Leachate, Ammonium, zeolite

I. INTRODUCTION

ORGANIC contaminant and ammoniacal nitrogen are two of the problematic parameters in landfill leachate treatment [1]. A high concentration of ammoniacal nitrogen is also known to inhibit the biological degradation by the microorganism [2,3].

Landfills can produce a great amount of leachate containing highly concentrated NH_4- N which is ordinarily removed by the way of ex-situ treatment for bioreactor landfills. The methods for ammonia removal from stabilized leachate include ion exchange, air-stripping, breakpoint chlorination, chemical precipitation, reserve osmosis and biological nitrification-denitrification [4,5]. The most widely used method is adsorption onto the surface of activated carbon in wastewater treatment. The high cost of activated carbon has stimulated interest in examining the feasibility of using cheaper raw materials.

One of the characteristics that distinguish zeolites from other porous materials is their variety of pore sizes and shapes. Properties of zeolites, such as ion exchange, intercrystalline pores that discriminate between molecules of different dimension, strong acidic sites, and active reservoirs for metal-catalyzed reactions have earned them extensive industrial uses. Zeolites are among the most important inorganic cation exchangers. Zeolites have large empty spaces, or cages, within their structures that can accommodate large cations, such as Na^+, K^+, Br^+, Mg^{2+} and Ca^{2+}, and even relatively şarge molecules and cationic groups, such as water, ammonia, carbonate ions, and nitrate ions.

Zeolites have high cation exchange selectivities, good resistance to temperature and ionizing radiations, and excellent compatibility with the environment.

Therefore, zeolites are widely used in modern technology as selective adsorbents, molecular sieves and particularly as catalysts [6].

The aim of this study is to investigate the capacity Manisa-Gordes zeolite for the NH_4-N removal from landfill leachate. The effects of different experimental parameters on removal of NH_4-N from leachate were investigated.

II. MATERIALS AND METHODS

A. *Adsorbent*

The zeolite (clinoptilolite) samples used in this study were received from Rota Company in Gördes-Manisa Basin of Turkey. The reason for selecting zeolite as an adsorbent is its relatively moderate surface area and exceptionally high and selective ion-exchange capacity. It is mineralogical content is mainly by clinoptilolite (85%) and other components are feldspar (10%), and clay (5%) [7]. The characteristic of natural zeolite is given the previous study [8].

The chosen zeolite was ground and classified -20+35 mesh size. Then it washed with distilled water to remove very fine particles and dried at 35-60°C to remove moisture. Since NH_4-N ion removal by using natural zeolite was aimed, preconditioning with 1 N NaCl and 2 N NaCl for 24 h, at 200 rpm and at 70°C.

B. *Characteristics of the leachate*

Samples of leachate water were taken several times during a period of two years at the Yilanlidere landfill in Samsun, Turkey. The characteristic of leachate is given the previous study [8].

III. RESULT AND DISCUSSION

A. *Effect of adsorbent dosage*

In order to investigate the influence of adsorbent dosage on adsorption of NH_4-N, series of experiment were undertaken for a wide range of dosage of natural zeolite. Prior to use, zeolite samples were sieved to a size of (-20+35 mesh). Then, the samples were treated with 1 N NaCl and 2 N NaCl solutions to saturate the exchange sites with sodium ions. Constant conditions were used throughout, namely, the agitation speed was 200 rpm, the temperature was 25°C and

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the initial NH_4-N concentration was maintained constant. The comparation of experimental for these systems in presented in Fig 1.

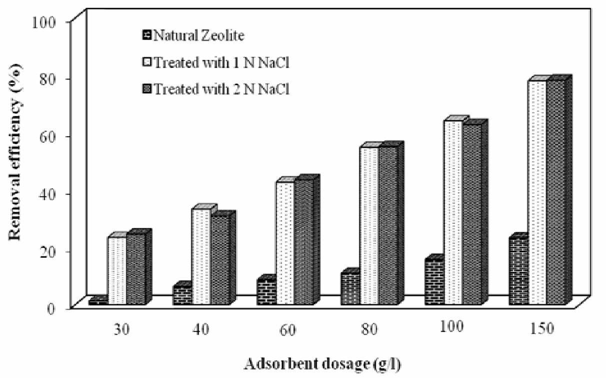

Fig. 1 Effect of adsorbent dosage on the adsorption of NH_4-N

These figure shows that the removal of NH_4-N increases with the increase both modify of zeolite and adsorbent dosage. The NH_4-N removal efficiencies of modified zeolite with 2 N NaCl varied from 25 to 78% at adsorbent concentrations of 30-150 g/l. As shown in Fig.1, the uptake of NH_4-N hasn't changed significiantly between 100 g/l and 150 g/l of adsorbent dosage. Therefore the optimal adsorbent dosage of 100 g/l of modified zeolite with 2 N NaCl was chosen.

B. *Effect of contact time*

Fig. 2 shows the plot of NH_4-N removal against contact time at initial concentration of 1386 mg/l. The rate of NH_4-N removal was found to be very rapid during the initial 30 min and to remain nearly constant thereafter.

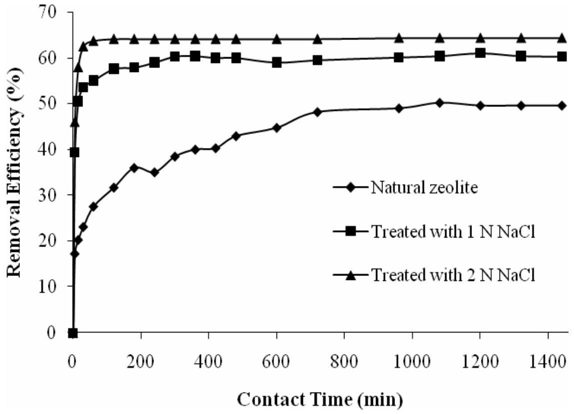

Fig. 2 Effects of contact time on the removal of NH_4-N (T=25^{o}C; NH_4-N conc= 1386 mg/L; pH=8.3; agitation rate: 200 rpm)

No significant change in NH_4-N removal was observed after about 12 h for natural zeolite, 4 h for treated with 1 N NaCl, 1 h for treated with 2 N NaCl. The NH_4-N removal efficiencies reached up to 48%, 60% and 64% for Natural zeolite, Treated with 1 N NaCl - zeolite and Treated with 2 N NaCl – zeolite, respectively. Therefore, it can be said that the removal of NH_4-N by Treated with 2 N NaCl - zeolite was found better than treated with 1 N NaCl - zeolite or Natural zeolite. For this, all experiments were carried out by equilibrium time of 1 h. Effects of contact time on the removal of NH_4-N are shown Fig. 2.

C. *Effect of initial concentration with contact time*

The initial concentration of adsorbate solution is very important. The rate of NH_4-N uptake by zeolite from the leachate solution was investigated to determine the optimum time required for the NH_4-N – zeolite system to reach equilibrium. The initial NH_4-N concentration was determined and amount of adsorbed NH_4-N in each set was calculated as a function of contact time. The results of the analysis of the effects of NH_4-N concentration on the removal are shown in Fig. 3. The adsorption rate of NH_4-N by zeolite was initially fast at the first 1 h, depending on the initial NH_4-N concentration in the leachate then decreased with increasing contact time. The data clearly showed the NH_4-N removal capacity of zeolite increased with the decreased of initial NH_4-N concentration in the leachate.

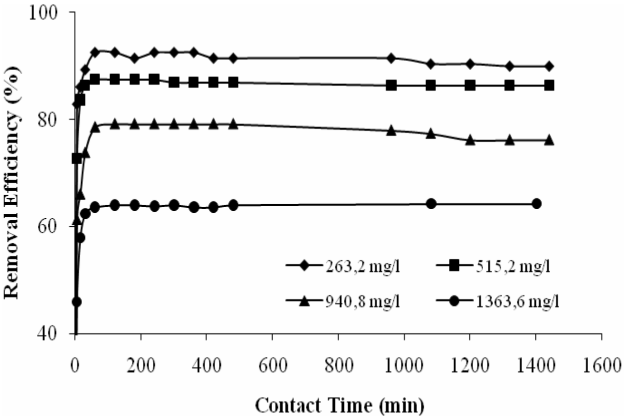

Fig. 3 Effect of initial concentration in the leachate on adsorption capacity

D. *Kinetic models*

Different kinetic models described below were used to describe NH_4^+ adsorption by natural zeolite. The goodness of conformity between experimental data and model predicted values was expresed by coefficient of determination (R^2). A relatively high r^2 value indicated that model successfully described the kinetics of NH_4^+ adsorption by natural zeolite [9]. Three kinetic models, Elovich model [10]., intraparticle diffusion model [11]. and pseudo-second order model [13]. were used to investigate the adsorption of NH_4-N on zeolite.

The effect of the initial NH_4-N concentrations and modification were investigated to find the best kinetic model. As shown Table 1, The experimental data fitted well to the pseudo-second-order kinetic model for the whole parameters.

TABLE I
KINETIC PARAMETERS FOR THE REMOVAL OF NH_4-N BY ZEOLITE

Pseudo-second order kinetic model

	qe_2 (mg g^{-1})	k_2 (g.mg^1min^{-1})	R^2
Initial Concentration			
263 mg/l	2.34	-0.070	0.99
515 mg/l	4.45	-0.186	1.00
941 mg/l	7.19	-0.025	0.99
1363 mg/l	8.77	0.076	1.00
Modification			
Natural Zeolite	7.15	0.0022	0.99
Treated with 1N NaCl	8.40	0.040	0.99
Treated with 2N NaCl	8.77	0.076	1.00

E. Adsorption equilibrium study

The procedure for the determination of the adsorption isotherms of the NH_4-N onto zeolite was described in the first part of this study. To optimize the design of an adsorption system for the adsorption of adsorbates, it is important to establish the most appropriate correlation for the equilibrium curves [14]. The successful representation of solute from solution onto an adsorbent depends upon a good description of the equilibrium seperation between the two phases. Adsorption equilibrium is established when the amount of solute being adsorbed onto the adsorbent is equal to the amount being desorbed. At this point, the equilibrium solution concentration remains constant. By plotting solid phase concentration against liquid phase concentration graphically it is possible to depict the equilibrium adsorption isotherm [15]. Various isotherm equations have been used to describe the equilibrium nature of adsorption. In this study, the sorption of NH_4-N by Gordes-zeolite were analysed by Langmuir [16,17]., Freundlich and Tempkin isotherm models [18].

Ammonium removal capacities for zeolite were studied with adsorption isotherms. For the effective utilization of a natural zeolite as an adsorbent, it is essential to have chemicals models that help to describe accurately NH_4-N equilibrium.

The corresponding correlation coefficients and the isotherm constants were calculated and presented in Table 4. However zeolite has multi ion exchange sites, our result showed that the Langmuir equation represents the sorption process very well. This result is in agreement with various researchers who used Langmuir equation to represent NH_4-N removal by clinoptilolite [5,19]. Values of q_m, which is defined as the total capacity of sorbent, at different temperatures, particle sizes, and agitation speeds have calculated from the Langmuir plots.

As a result, the isotherm models of Langmuir and Tempkin fitted the experimental data better than the rest of models. These models allowed for the linear profile of the isotherm giving the highest value of R^2.

A sorption isotherm is characterized by certain constants the values of which express the surface properties and affinity of the sorbent. The magnitude of the exponent n gives an indication of the favorability of sorption. It is generally stated that values of n in the range 2–10 represent good, 1–2 moderately difficult, and less than 1 poor adsorption characteristics [20]. The studied material is not good sorbent for NH_4-N ($1.67< n<1.96$).

The Langmuir model makes several assumptions, such as monolayer coverage and constant adsorption energy while the Freundlich equation deals with heterogeneous surface adsorption.

From Table 2, if just the Langmuir is used for comparison, Langmuir was more suitable for the experimental data than was the Freundlich isotherm because of the higher value of the coefficient of determination. Among the tested three-parameter equations, the better and perfect representation of the experimental results of the adsorption isotherms is obtained using the Langmuir–Tempkin model (Table 2).

TABLE II
THE COMPARISON OF THE SORPTION CONSTANTS OBTAINED AT DIFFERENT TEMPERATURE CONDITIONS

Freundlich	K_F	*1/n*	R^2
25ºC	0.23	1.67	0.89
40ºC	0.39	1.88	0.82
60ºC	0.36	1.85	0.98
Langmuir	q_m	K_L	R^2
25ºC	9.07	0.66	0.96
40ºC	8.77	0.98	0.96
60ºC	9.30	0.99	0.95
Tempkin	K_t	*B*	R^2
25ºC	0.09	1.97	0.97
40ºC	0.14	1.87	0.97
60ºC	0.17	1.75	0.93

IV. CONCLUSIONS

The following conclusions can be drawn from the results of experiments in this study:

1. The NH_4-N removal capacity of Gordes zeolite increases with the increase of initial NH_4-N concentrations in the landfill leachate solution.
2. The kinetics of the process indicates a minimum adsorption time in 1, 4 and 12 h to equilibrium conditions. The pseudo second order equation is capable of modelling the adsorption regardless of the type and amount of zeolite. The pseudo-second order kinetic reaction model found to be the best correlation of the data for NH_4-N removal from leachate using zeolite.

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3. The results obtained using the three-parameter equations show that the best-fitted adsorption isotherm models were determined to be in the order: Langmuir - Tempkin > Freundlich

The present study shows that Gordes zeolite is an effective sorbent for the removal of NH_4-N from landfill leachate.

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