

A comparative study of linear and non-linear regression analysis for ammonium exchange by clinoptilolite zeolite

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Abstract

Ammonium ion exchange from aqueous solution using clinoptilolite zeolite was investigated at laboratory scale. Batch experimental studies were conducted to evaluate the effect of various parameters such as pH, zeolite dosage, contact time, initial ammonium concentration and temperature. Freundlich and Langmuir isotherm models and pseudo-second-order model were fitted to experimental data. Linear and non-linear regression methods were compared to determine the best fitting of isotherm and kinetic model to experimental data. The rate limiting mechanism of ammonium uptake by zeolite was determined as chemical exchange. Non-linear regression has better performance for analyzing experimental data and Freundlich model was better than Langmuir to represent equilibrium data.

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1. Introduction

Wastewater generated from industrial and domestic use contains many toxic pollutants. Ammonia is one of these toxic pollutants creating many problems. Ammonia nitrogen decreases the dissolved oxygen required for aquatic organisms, and also accelerates the corrosion of metals and construction materials [1]. The traditional processes used for ammonia removal are biological nitrification–denitrification and air stripping but recent efforts have been made to discover new economically feasible and environmentally friendly treatment alternatives. Among several removal technologies, ion exchange with natural minerals has great importance due to the ease of operation and comparable low cost of application [2–4]. In the aqueous solution, ammonia can exist in either the non-ionized form (NH₃) and/or ionised form (NH₄⁺) depending on the pH and temperature. Of these two forms of ammonia, only the ionised one can be removed by the ion-exchange process [5].

Zeolite minerals are mainly composed of aluminosilicates with a three dimensional framework structure bear-

ing Al-octahedra and Si-tetrahedra. Zeolite is a silica-rich material occurring in natural abundance especially in volcanic areas and the typical unit cell formula is given as Na₆[(AlO₂)₆(SiO₂)₃₀]·24H₂O [6]. Three dimensional crystal structure of zeolite contains two-dimensional channels which embody some ion exchangeable cations such as Na⁺, K⁺, Ca²⁺ and Mg²⁺ [7]. Exchange properties of these cations have been utilized for uptake of ammonium by clinoptilolite zeolite and it has been found very effective for removing ammonia from aqueous solution [8–10].

In literature, the linear regression analysis has been the most commonly used technique to determine the best-fit isotherm and kinetic models for ammonia removal [10–12]. Least squares method is used for finding the parameters of the models, but linear regression is criticized since it results in different linearized forms. In recent years, several researchers have used non-linear regression to analyze isotherm models for ion exchange process [13–15].

In this study, we investigated the parameters effecting on the ammonium exchange by Turkish clinoptilolite zeolite. Four linearized types of Langmuir isotherm and pseudo-second-order kinetic models were used for linear regression analysis. In linear regression analysis, the least squares method was used to predict the parameters. Non-linear regression was performed using

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trial and error method with the help of solver add-in functions of Microsoft Excel software [16].

2. Material and methods

The clinoptilolite zeolite (CZ) was obtained from the Incal Company in Western Anatolia, Turkey. The CZ sample was crushed and classified to a size range of 0.3–0.6 mm then washed to remove undesirable materials, and finally dried in an oven at $100 \pm 5^\circ\text{C}$ for 24 h. CZ has following properties: pore diameter of 4×10^{-6} μm , purity of 92%, bed porosity of 40%, density of 2.15 g/cm^3 and apparent density of 1.30 g/cm^3 . Chemical composition of CZ is given in Table 1 [17].

In batch experiments, 1 g of the CZ was weighed into flasks containing 50 ml of solution with different ammonium concentrations in the range of 20 to 100 mg/l. This mixture was agitated in a temperature-controlled orbital shaker at a constant speed of 200 rpm. Samples were withdrawn at various time intervals between 5 and 50 min and equilibrium concentrations of NH_4^+ were determined with colorimetric method [18]. pH was adjusted by the addition HCl or NaOH and the effect of pH was studied over pH range of 4–10. The effect of temperature on the ammonium exchange process was investigated by determining the isotherms at 303, 308 and 313 K.

Ammonium exchange capacity (q_e) was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

where q_e (mg/g) is the amount of ammonium exchanged ion at equilibrium, C_0 and C_e the initial and equilibrium concentrations of ammonium in solution (mg/l), respectively. V (l) the solution volume and M (g) is the CZ weight.

Linear and non-linear regressions were compared to obtain the optimum sorption kinetic and isotherm parameters. A trial error procedure was employed for non-linear methods using the solver add-in functions of Microsoft Excel software. In trial error procedure, isotherm and kinetic parameters were determined by maximizing the values of coefficient of determination.

The least squares method was used to analyze the linear forms of kinetic and isotherm models.

Table 1
Chemical constituent of clinoptilolite zeolite

Composition	Percent
SiO_2	70.00
Al_2O_3	14.00
Fe_2O_3	0.75
K_2O	2.30
MgO	1.15
Na_2O	0.20
CaO	2.50
TiO_2	0.05
P_2O_5	0.02
SO_3	0.01
Loss of ignition	9.02

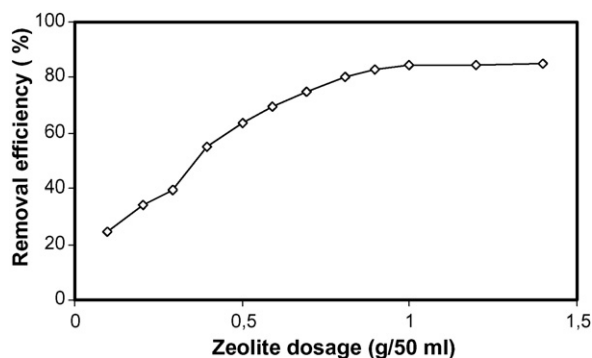


Fig. 1. Effect of zeolite dosage on the exchange of NH_4^+ ($T=303 \text{ K}$; agitation speed = 200 rpm; $C_0 = 20 \text{ mg/l}$).

Values of coefficient of determination (R^2) were used in order to find the fitting degrees of isotherm and kinetic models with experimental data. Coefficient of determination is defined as [14]:

$$R^2 = \frac{\sum (q_{\text{cal}} - q_{\text{m exp}})^2}{\sum (q_{\text{cal}} - q_{\text{m exp}})^2 + (q_{\text{cal}} - q_{\text{m exp}})^2} \quad (2)$$

where q_{exp} (mg/g) is the amount of ammonium ion exchanged by zeolite obtained from experiment, q_{cal} the amount of ammonium ion obtained by kinetic and isotherm models and $q_{\text{m exp}}$ the average of q_{exp} (mg/g).

3. Results and discussion

3.1. The effects of parameters on the equilibrium of ammonium ion exchange

The effect of CZ dosage on the uptake of NH_4^+ was studied and shown in Fig. 1. From the figure it was observed that, the removal rate of ammonium increased with increase in CZ dosage. The removal rate of ammonium increased from 24.7% to 84.7% for an increase of CZ dosage from 0.2 to 1 g per 50 ml. This was probably due to greater surface area and availability of more exchange site.

The effect of pH on NH_4^+ exchange was studied over a pH range of 4–10 and the results are shown in Fig. 2. The highest exchange capacity was achieved at pH 6. In the range of 5 and 8, pH has a little effect on the ammonium exchange and it can

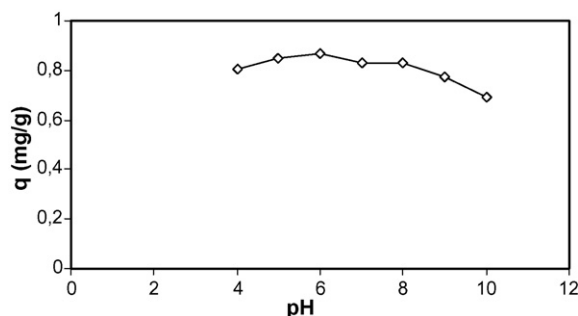


Fig. 2. Effect of pH on the exchange of NH_4^+ by CZ ($T=303 \text{ K}$; agitation speed = 200 rpm; CZ dosage = 1 g/50 ml; $C_0 = 20 \text{ mg/l}$).

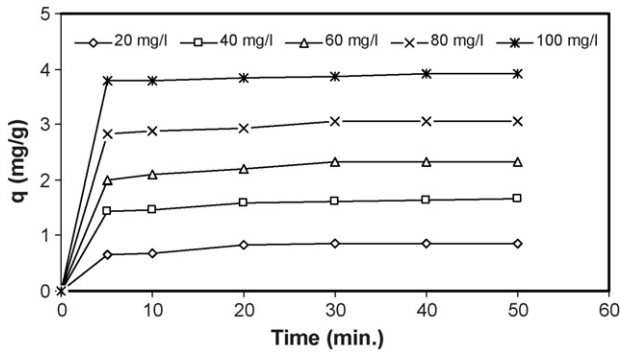


Fig. 3. Effect of concentration and contact time on ammonium exchange by CZ ($T = 303$ K; agitation speed = 200 rpm; pH 6; zeolite dosage = 1 g/50 ml).

be concluded that neutral pH is favorable for ammonium uptake by CZ. For the pH value of above 8 and below 5, ammonium exchange capacity was decreased rapidly. This result is consistent with the results in literature [19,20]. At higher pH values, ammonium ions are transformed to aqueous ammonia. Lower values of ammonium removal below pH 5 is due to competition of H^+ and NH_4^+ ions for the exchange sites in the CZ surfaces [21].

In order to find out the optimum contact time, ammonium ion exchange by CZ was studied at different initial NH_4^+ concentrations between 20 and 100 mg/l. It is evident from Fig. 3 that uptake of NH_4^+ by CZ was more rapid within first 5 min of contact time. The removal rate of ammonium gradually decreased with increased in contact time and reached equilibrium at 30 min for all concentrations studied. Initially the rate of ammonium uptake was higher because all sites on CZ were vacant and solute concentration was high, but decreasing in sorption sites reduced the uptake rate. Maximum capacity was obtained 3.92 mg/g at equilibrium for the concentration of 100 mg/l.

The effect of temperature on ammonium exchange was studied at 303, 308 and 313 K, and the results are shown in Fig. 4. As shown in the figure, all values were almost the same and temperature effect was not significant on the exchange capacity of ammonium.

The free energy change (ΔG°) is used to distinguish the spontaneity of the adsorption process, and the higher negative value

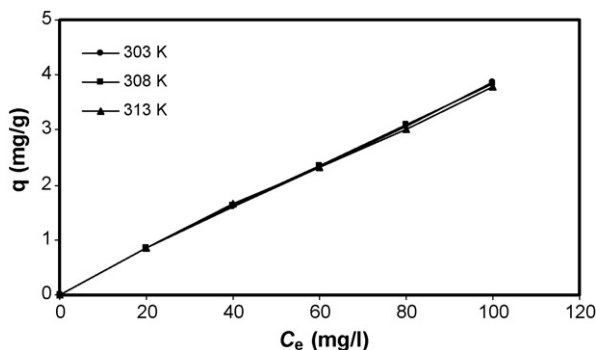


Fig. 4. Effect of temperature on the ammonium exchange by zeolite (agitation speed = 200 rpm; zeolite dosage = 1 g/50 ml; pH 6).

Table 2

The values of free energy change at various temperatures (kJ/mol)

	303 K	308 K	313 K
20 mg/l	-4.31	-4.75	-4.63
40 mg/l	-3.61	-3.90	-4.00
60 mg/l	-3.11	-3.22	-3.14
80 mg/l	-2.95	-3.12	-2.88
100 mg/l	-2.90	-3.10	-2.88

suggests a more energetically favorable adsorption [22]:

$$\Delta G^\circ = -RT \ln K_C \quad (3)$$

$$K_C = \frac{C_A}{C_S} \quad (4)$$

where C_A and C_S (mg/l) are the equilibrium concentration of NH_4^+ on the CZ and solution, respectively, K_C the equilibrium constant, T the solution temperature (K) and R is the gas constant. The negative values of ΔG° in Table 2 suggest that ammonium exchange by CZ is spontaneous at all conditions studied. Ammonium exchange by CZ is less favorable at higher concentrations since lower concentrations have more negative ΔG° values.

3.2. Rate limiting

Determination of the rate limiting steps involving in sorption process is necessary for practical application and designing of sorption reactors [23]. The rate of ion exchange is governed by film diffusion, particle diffusion or chemical exchange [24]. In literature, it is proposed that rate of ion exchange is controlled by chemical exchange if the relationship between $\log(1 - q_t/q_\infty)$ and time is linear [25–27]. In this study q values at 50 min. were accepted as q_∞ values. As shown in Fig. 5, linearity of $\log(1 - q_t/q_\infty)$ versus time indicates that rate limiting step of ammonium uptake by CZ is chemical reaction and increasing of temperature increases the effect of chemical reaction. Similar result was found by Biserka and Subotic [28] for the Cd exchange by zeolite.

3.3. Kinetic study

Researchers found that if rate of a reaction is controlled by chemical exchange, pseudo-second-order model has best cor-

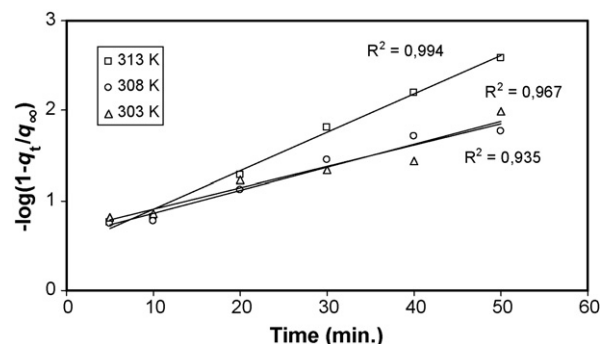


Fig. 5. Rate limiting mechanism of ammonium exchange by clinoptilolite zeolite.

Table 3
Linear forms of pseudo-second-order kinetic model

	Linear formula	Plot	Parameters
Type 1	$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t$	t/q_t vs. t	$q_e = 1/\text{slope}$, $k = \text{slope}^2/\text{intercept}$
Type 2	$\frac{1}{q_t} = \left(\frac{1}{kq_e^2}\right)\frac{1}{t} + \frac{1}{q_e}$	$1/q_t$ vs. $1/t$	$q_e = 1/\text{intercept}$, $k = \text{intercept}^2/\text{slope}$
Type 3	$q_t = q_e - \left(\frac{1}{q_e}\right)\frac{q_t}{t}$	q_t vs. q_t/t	$q_e = \text{intercept}$, $k = -1/(\text{intercept} \times \text{slope})$
Type 4	$\frac{q_t}{t} = kq_e^2 - kq_eq_t$	q_t/t vs. q_t	$q_e = -\text{intercept}/\text{slope}$, $k = \text{slope}^2/\text{intercept}$

relation with experimental kinetic data [29–31]. The pseudo-second-order kinetic model is expressed as below [29]:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{5}$$

where k is the rate constant of second-order model (g/mg min) and q_e (mg/g) is the amount of ammonium uptake at equilibrium. For boundary conditions ($t=0-t$ and $q_t=0-q_e$), Eq. (5) becomes as below

$$q_t = \frac{t}{1/kq_e^2 + t/q_e} \tag{6}$$

Eq. (6) can be linearized as four different types as shown in Table 3 [14]. The least squares method was applied to obtain the best-fit linear formula and predict parameters values. The parameters estimated using linear regression resulted different values for each linear formula. Different values in Table 4 are due to transformations of non-linear isotherm equations to linear forms implicitly alter their error structure and may also violate the error variance and normality assumptions of standard least

Table 4
Pseudo-second-order kinetic model parameters estimated by linear regression

	q_e (mg/g)	k (g/mg min)	R^2
Type 1			
20 mg/l	0.858	0.863	0.695
40 mg/l	1.722	0.359	0.852
60 mg/l	2.379	0.366	0.934
80 mg/l	3.094	0.485	0.821
100 mg/l	3.944	0.526	0.643
Type 2			
20 mg/l	0.868	0.645	0.820
40 mg/l	1.675	0.618	0.848
60 mg/l	2.359	0.435	0.924
80 mg/l	3.064	0.699	0.772
100 mg/l	3.892	1.553	0.474
Type 3			
20 mg/l	0.869	0.646	0.820
40 mg/l	1.678	0.609	0.853
60 mg/l	2.361	0.429	0.926
80 mg/l	3.065	0.694	0.775
100 mg/l	3.892	1.544	0.477
Type 4			
20 mg/l	0.892	0.493	0.860
40 mg/l	1.696	0.503	0.881
60 mg/l	2.373	0.392	0.934
80 mg/l	3.091	0.527	0.823
100 mg/l	3.937	0.727	0.662

squares [13]. The best fitting was obtained by using the type 4 formula since it had highest R^2 values for all concentration studied.

For non-linear regression, trial and error procedure was used to maximize the coefficient of determination with the help of Microsoft Excel software. The obtained values were compared with the results of linear regression. As shown in Table 5, the results are close to each other but non-linear regression has better correlation with experimental data.

3.4. Equilibrium isotherms

The study of equilibrium is essential in supplying the fundamental information required for the design and operation of sorption process. In literature, Langmuir and Freundlich isotherm models have been most commonly used to analysis the equilibrium data.

The Langmuir isotherm model [32] assumes that the sorption takes place at specific homogeneous sites within the adsorbent. Langmuir equation can be expressed as

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{7}$$

Where, q_m (mg/g) and K_L (l/mg) are the constants of the Langmuir equation. Langmuir isotherm model can be linearized into at least four different types as shown in Table 6 [15].

The obtained values using linear and non-linear regression are listed in Table 7. All linear equations resulted different parameter and R^2 values. While the lowest correlation was

Table 5
Comparison of linear regression analysis data obtained from Type 4 with non-linear regression data of Pseudo-second-order model and non-linear regression analysis of pseudo-second model

	q_e (mg/g)	k (g/min mg)	R^2
Non-linear			
20 mg/l	0.896	0.463	0.862
40 mg/l	1.700	0.479	0.882
60 mg/l	2.376	0.381	0.935
80 mg/l	3.094	0.511	0.824
100 mg/l	3.938	0.705	0.662
Linear			
20 mg/l	0.892	0.493	0.860
40 mg/l	1.696	0.503	0.881
60 mg/l	2.373	0.392	0.934
80 mg/l	3.091	0.527	0.823
100 mg/l	3.937	0.727	0.662

Table 6
Linear forms of Langmuir isotherm model

	Linear formula	Plot	Parameters
Type 1	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L q_m}$	C_e/q_e vs. C_e	$q_m = 1/\text{slope}$, $K_L = \text{slope}/\text{intercept}$
Type 2	$\frac{1}{q_e} = \left(\frac{1}{K_L q_m}\right) \frac{1}{C_e} + \frac{1}{q_m}$	$1/q_e$ vs. $1/C_e$	$q_m = 1/\text{intercept}$, $K_L = \text{intercept}/\text{slope}$
Type 3	$q_e = q_m - \left(\frac{1}{K_L}\right) \frac{q_e}{C_e}$	q_e vs. q_e/C_e	$q_m = \text{intercept}$, $K_L = -1/\text{slope}$
Type 4	$\frac{q_e}{C_e} = K_L q_m - K_L q_e$	q_e/C_e vs. q_e	$q_m = -\text{intercept}/\text{slope}$, $K_L = -\text{slope}$

Table 7
Langmuir and Freundlich constants and coefficient of determinations estimated by linear and non-linear regression analysis

	Langmuir			Freundlich		
	q_m	K_L	R^2	n_f	K_f	R^2
Linear				1.395	0.375	0.993
Type 1	5.766	0.055	0.928			
Type 2	7.734	0.046	0.496			
Type 3	6.455	0.047	0.959			
Type 4	7.363	0.039	0.976			
Non-linear	11.252	0.021	0.988	1.314	0.333	0.996

obtained using Type 2, Type 4 has best fitting with experimental data.

The Freundlich isotherm [33] is the earliest known relationship describing the sorption equation. This isotherm has an assumption that sorption takes place at a heterogeneous surface with a non-uniform distribution and is given as follows. The formula of Freundlich model is given as

$$q_e = K_f C_e^{(1/n_f)} \quad (8)$$

where q_e is the equilibrium ammonium ion exchange of CZ, C_e the concentration of solution at equilibrium, and K_f and n_f are the empirical constants which are indicators of sorption capacity and adsorption intensity, respectively.

The linearized form of the Freundlich model is given in Eq. (9):

$$\ln q_e = \ln K_f + \left(\frac{1}{n_f}\right) \ln C_e \quad (9)$$

K_f and n_f are the Freundlich constants and obtained from the intercept and slope of linear plot of $\ln q_e$ versus $\ln C_e$.

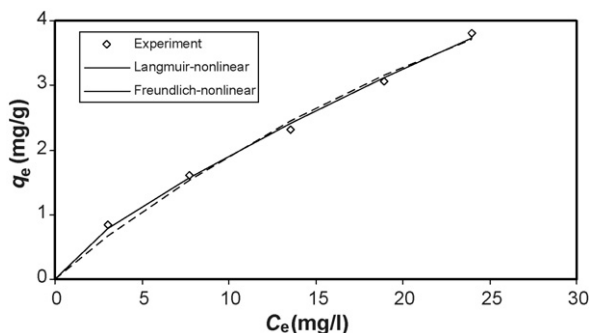


Fig. 6. Comparison of isotherm models for ammonium exchange.

Equilibrium data were analyzed using linear and non-linear forms of Freundlich isotherm model and the R^2 values were estimated as 0.993 and 0.996 for linear and non-linear regression, respectively. These figures show that non-linear regression has better fit than linear regression.

Non-linear regression of Langmuir and Freundlich isotherm models are compared and shown in Fig. 6. As shown in the figure, Freundlich model is better than Langmuir to represent the equilibrium experimental data.

4. Conclusions

In this study, parameters affecting on equilibrium of ammonium exchange by zeolite and applicability of linear and non-linear regression for estimating kinetic and isotherm models were investigated. Exchange capacity of ammonium ion by clinoptilolite increased with initial ammonium concentration and contact time. pH 6 was found as the optimum value for ammonium exchange. The effect of temperature was not significant and lower concentrations are more favorable according to values of free energy change. The chemical exchange was found as the rate limiting of ammonium exchange by zeolite.

Linear and non-linear regression methods were compared to evaluate the experimental data with Pseudo-second-order kinetic model. Four linearized types of the model were used for linear regression and compared using coefficients of determinations. Non-linear regression exhibited higher coefficient of determination values for isotherm and kinetic analysis than the linear regression.

The Freundlich and Langmuir isotherm models were evaluated using linear and non-linear regression analysis. Values of coefficient of determination showed that Freundlich has better performance than Langmuir for representing the equilibrium data. Linear regression for the same kinetic and isotherm model resulted different values. This was due to linearization method which changes the error distribution. Non-linear regression provided higher correlation with experimental data for both kinetic and isotherm analysis and this is well agreement with the results in literature.

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