

Application of nonlinear regression analysis for ammonium exchange by natural (Bigadiç) clinoptilolite

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Abstract

The experimental data of ammonium exchange by natural Bigadiç clinoptilolite was evaluated using nonlinear regression analysis. Three two-parameters isotherm models (Langmuir, Freundlich and Temkin) and three three-parameters isotherm models (Redlich–Peterson, Sips and Khan) were used to analyse the equilibrium data. Fitting of isotherm models was determined using values of standard normalization error procedure (SNE) and coefficient of determination (R^2). HYBRID error function provided lowest sum of normalized error and Khan model had better performance for modeling the equilibrium data. Thermodynamic investigation indicated that ammonium removal by clinoptilolite was favorable at lower temperatures and exothermic in nature.

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1. Introduction

The release of ammonium into the environment in effluent from industrial and domestic sources has become a major concern in wastewater treatment. Among several removal technologies, ion exchange with natural clays has great importance due to the ease of operation and comparable low cost of application. Most of the clays, which are hydrated aluminum–silicate minerals, have shown affinity to remove ammonium from aqueous solution [1–3].

Clinoptilolite is one of the most abundant natural zeolite species that occurs in relatively large minerable sedimentary deposits in sufficiently high purity in many parts of the world [4]. Ammonia removal from aqueous solution by using clinoptilolite has been investigated by many researchers [5–6]. The abundance and availability of clinoptilolite mineral reserves in Turkey as a raw material source and its relatively low cost, guarantee its continued utilization in the future.

In literature, the linear regression analysis has been frequently preferred to evaluate the fit of experimental data and isotherm

models for ion exchange by clinoptilolite. In recent years, several studies have been performed for the comparison of linear and nonlinear regression analysis for ion exchange systems. Researchers found that linear regression analysis insufficient to explain the experimental data and nonlinear regression has better performance for describing the ion exchange systems [7–8].

The scope of this study is to investigate ammonium removal from aqueous solution to find out isotherm parameters and thermodynamic profile of clinoptilolite–ammonium system by using natural clinoptilolite. Nonlinear optimization technique was conducted to determine the isotherm parameters of ammonium exchange by natural clinoptilolite. Five error functions were used to evaluate accuracy of nonlinear regression analysis using trial and error method with the help of solver add-in functions of Microsoft Excell software.

2. Materials and methods

2.1. Experimental design

The clinoptilolite sample used as an adsorbent was taken from the deposits in Bigadiç, Turkey and was crushed and sieved into a diameter of 0.3–0.6 mm. The chemical composition of the sample is given in Table 1 [9]. Prior to the experiments, the sample was washed with distilled water to remove the surface dust and

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Table 1
The chemical composition of Bigadiç clinoptilolite [9]

Constituent	Weight (%)
SiO ₂	64.99
Al ₂ O ₃	9.99
K ₂ O	1.95
CaO	3.51
Na ₂ O	0.18
MgO	1.01
Fe ₂ O ₃	3.99
H ₂ O	14.47

dried in an oven at 303 K. Experiments of ammonium exchange onto clinoptilolite were carried out using batch mode in Galenkamp orbital shaker. In batch experiments, 0.4 g of adsorbent weighed into conical flasks containing 100 ml ammonium solution. Synthetic ammonium solutions were prepared by adding required NH₄Cl salt (Merck quality) to obtain concentration range between 5 and 150 mg/l. The flasks were shaken at 200 rpm for 12 h and samples were taken for measurement of aqueous-phase ammonium concentration. Preliminary tests confirmed that a 30–60 min contact time was enough to reach a steady-state ammonium concentration [10]. Ammonium concentrations remained in the solution were determined using Nessler method [11].

The effect of temperature on the ammonium exchange process was investigated at 296, 383, 323 and 343 K. For all experiments, natural pH (6.5) is preferred since it is in the range of optimum pH values reported in the literature [8,10].

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

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

where C_0 and C_e are the amount of initial and retained ammonium ion in the solution at equilibrium (mg/l), respectively, V is the solution volume (ml) and m is the weight of adsorbent (g).

2.2. Isotherm models

In literature Langmuir isotherm model has been widely used for modeling equilibrium data. It is represented as [12]:

$$q_e = \frac{Q_0 a_L C_e}{1 + a_L C_e} \quad (2)$$

where Q_0 (mg/g) is the maximum amount of ammonium uptaken and a_L (l/mg) is the constant of the Langmuir model.

The empirical Freundlich equation is based on a heterogeneous surface is given by [13]:

$$q_e = K_f C_e^{1/n} \quad (3)$$

where K_f and n are Freundlich constants which are indicators of adsorption capacity and adsorption intensity, respectively.

Temkin isotherm assumes that decrease in the heat of adsorption is linear and the adsorption is characterized by a uniform distribution of binding energies. Temkin isotherm is expressed

by the following equation [14].

$$q_e = \frac{RT}{b} \ln(K_T C_e) \quad (4)$$

where K_T is equilibrium binding constant (l/g), b is related to heat of adsorption (J/mol), R is the gas constant (8.314×10^{-3} kJ/K mol) and T is the absolute temperature (K).

Redlich–Peterson isotherm approximates to Henry's law at low sorbate concentrations, and at high concentrations it behaves like the Freundlich isotherm. It is given as [15]:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^\beta} \quad (5)$$

where K_R (l/g) and a_R (l/mg) are Redlich–Peterson isotherm constants and β is the exponent which lies between 0 and 1.

Khan et al. [16] have suggested a generalized isotherm for pure solutions. Khan isotherm is given as:

$$q_e = \frac{q_m b_K C_e}{(1 + b_K C_e)^{a_K}} \quad (6)$$

q_m and b_K are the Khan model constant and a_K is the Khan model exponent.

Sips isotherm is a combination of the Langmuir and Freundlich models and expected to describe heterogeneous surfaces much better. At low sorbate concentrations it reduces to a Freundlich isotherm, while at high sorbate concentrations it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm. The model can be written as [17]:

$$q_e = \frac{q_m a_s C_e^{1/n}}{1 + a_s C_e^{1/n}} \quad (7)$$

where q_m is monolayer adsorption capacity (mg/g) and a_s is Sips constant related to energy of adsorption.

2.3. Error functions

The sum of the squares of the errors (SSE) is used widely in literature but it has one major drawback. SSE provides best fit at the higher concentration data as magnitude of the errors and the square of the errors will increase as concentration increases.

$$SSE = \sum_{i=1}^n (q_{e_{cal}} - q_{e_{exp}})^2 \quad (8)$$

The sum of the absolute errors (SAE) is similar to SSE error function.

$$SAE = \sum_{i=1}^n |q_{e_{cal}} - q_{e_{exp}}| \quad (9)$$

The average relative error (ARE) function minimizes the fractional error distribution across the entire concentration range.

$$SAE = \frac{100}{n} \sum_{i=1}^n \frac{|q_{e_{cal}} - q_{e_{exp}}|}{q_{e_{exp}}} \quad (10)$$

The hybrid fractional error function (HYBRID) was developed by Porter et al. [18] in order to improve the fit of the SSE

function at low concentration values by dividing it by the experimental data. In addition, a divisor was included as a term for the number of degrees of freedom for the system—the number of data points minus the number of parameters within the isotherm equation.

$$\text{HYBRID} = \frac{100}{p-n} \sum_{i=1}^n \left[\frac{(q_{e_{\text{exp}}} - q_{e_{\text{cal}}})^2}{q_{e_{\text{exp}}}} \right] \quad (11)$$

Marquardt's percent standard deviation (MPSD) error function [19] was similar to a geometric mean error distribution which was modified to allow for the number of degrees of freedom of the system. Instead of n as used in the ARE function the sum of the fractional errors is divided by $(n-p)$ where p is the number of parameters in the isotherm equation.

$$\text{MPSD} = 100 \times \left(\frac{1}{p-n} \sum_{i=1}^n \left[\frac{(q_{e_{\text{exp}}} - q_{e_{\text{cal}}})^2}{q_{e_{\text{exp}}}} \right] \right) \quad (12)$$

In function formulas $q_{e_{\text{exp}}}$ is the experimental data and $q_{e_{\text{cal}}}$ is data obtained from nonlinear modeling. Since each error function gives different values, in order to find out the best fit isotherm parameters sum of normalized errors (SNE) procedure was employed as described elsewhere [20,21].

2.4. Coefficient of determination

Coefficient of determination (R^2) was also used to evaluate the comparison of isotherm models with experimental data. Coefficient of determination is given as:

$$R^2 = \frac{\sum (q_{\text{mod}} - q_{\text{aexp}})^2}{\sum (q_{\text{mod}} - q_{\text{aexp}})^2 + \sum (q_{\text{mod}} - q_{\text{exp}})^2} \quad (13)$$

where q_{exp} (mg/g) is equilibrium value obtained from experiment, q_{mod} is calculated by isotherm model q_{aexp} is the average of q_{exp} .

3. Results and discussion

3.1. Nonlinear regression analysis

Values of standard normalization error (SNE) were used to assess best error function for selecting the isotherm model and calculating parameters. The calculated values of parameters and error analysis using nonlinear regression at 296 K are given in Tables 2 and 3. Figures in bold type indicate the minimum values of SNE for relevant error function.

HYBRID provided the best estimation of parameters for all two-parameters isotherm models due to the lowest SNE values (Table 2). The lowest SNE values were found as 3.800, 3.109 and 2.827 for Langmuir, Freundlich and Temkin models, respectively. Comparison of the results of three-isotherm models indicates that the lowest SNE values were obtained for RP and Sips models with HYBRID and for Khan model with SAE error function (Table 3). According to these figures, HYBRID error function was selected for evaluating the fitting of isotherm models to experimental data.

Table 2
SNE and error function values for two-parameters isotherm models at 296 K

	SSE	SAE	ARE	HYBRID	MPSD
Langmuir					
Q_0	15.725	15.027	14.622	15.207	14.518
a_L	0.055	0.058	0.066	0.061	0.068
SSE	0.770	1.247	1.399	0.922	1.552
SAE	2.237	2.069	1.999	2.227	2.281
ARE	5.151	4.894	3.456	4.247	3.764
HYBRID	2.201	2.740	2.133	1.806	2.321
MPSD	8.171	8.405	5.723	6.270	5.420
SNE	4.252	4.660	3.907	3.800	4.223
Freundlich					
K_f	2.172	2.209	1.389	1.855	1.588
$1/n$	0.413	0.411	0.527	0.456	0.503
SSE	2.383	2.442	8.281	3.271	6.588
SAE	3.761	3.556	6.761	4.480	5.847
ARE	11.158	11.079	11.528	9.981	9.973
HYBRID	11.445	12.211	16.714	8.541	11.475
MPSD	21.621	22.587	15.190	15.233	12.811
SNE	3.454	3.512	4.672	3.109	3.779
Temkin					
K_T	0.704	0.598	1.005	0.826	0.930
b	786.275	750.765	926.618	842.174	903.286
SSE	1.262	1.754	4.034	1.745	3.445
SAE	2.598	2.017	4.162	3.234	3.931
ARE	8.249	8.774	6.602	7.404	6.792
HYBRID	6.405	13.086	7.021	4.563	5.928
MPSD	16.454	25.461	10.022	10.815	9.370
SNE	3.013	3.919	3.683	2.827	3.394

Values of parameters were calculated for all temperatures studied and isotherm models were evaluated using HYBRID function. HYBRID and R^2 values in Tables 4 and 5 and equilibrium data in Figs. 1 and 2 indicated that experimental data have better fitting with three-parameters models than two-parameter models. Similar results were found by other researchers in literature [22,23].

Comparison of two-parameters isotherm models suggested that Langmuir model has lowest HYBRID error values and Temkin model has worst fitting degree with experimental data for all temperatures studied. Maximum exchanged ammonium ion (Q_0) was 15.207 mg/g at 296 K and decreased to 14.515 mg/g at 343 K. The values of K_f and K_T parameters of Freundlich

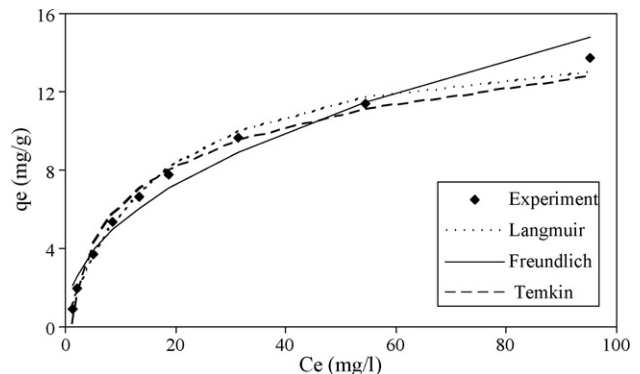


Fig. 1. Comparison of two-parameters isotherm models with experimental data (Temperature: 296 K).

Table 3
SNE and error function values for three-parameter isotherm models at 296 K

	SSE	SAE	ARE	HYBRID	MPSD
Redlich–Peterson					
K_R	1.269	1.261	1.246	1.230	1.224
a_R	0.183	0.179	0.175	0.169	0.167
β	0.825	0.827	0.829	0.835	0.837
SSE	0.068	0.084	0.083	0.071	0.072
SAE	0.606	0.501	0.492	0.588	0.592
ARE	1.206	1.055	0.963	1.111	1.128
HYBRID	0.207	0.233	0.222	0.194	0.194
MPSD	2.011	2.064	1.953	1.851	1.848
SNE	4.676	4.702	4.510	4.468	4.499
Khan					
q_m	7.950	7.941	7.950	8.062	7.884
b_k	0.143	0.143	0.144	0.140	0.144
a_K	0.772	0.770	0.771	0.775	0.769
SSE	0.052	0.058	0.062	0.053	0.053
SAE	0.527	0.468	0.488	0.532	0.542
ARE	1.140	1.066	1.065	1.171	1.170
HYBRID	0.174	0.184	0.202	0.173	0.175
MPSD	1.943	1.969	2.058	1.954	1.940
SNE	4.591	4.566	4.810	4.631	4.653
Sips					
q_m	19.116	17.378	17.000	18.163	17.620
a_s	0.069	0.069	0.070	0.068	0.068
$1/n$	0.782	0.844	0.851	0.822	0.844
SSE	0.160	0.281	0.394	0.184	0.222
SAE	0.965	0.954	0.974	0.948	1.005
ARE	2.233	1.351	1.342	1.632	1.475
HYBRID	0.516	0.518	0.668	0.405	0.434
MPSD	3.655	2.395	2.576	2.400	2.243
SNE	4.142	3.700	4.275	3.403	3.486

and Temkin models also decreased with increasing of temperatures.

Sips isotherm model has the highest error values in three-parameters isotherm models and the HYBRID values of R–P and Khan models are close to each other. Evaluating two models indicated that Khan model has better performance for fitting with experimental data.

Table 4
Comparison of two-parameter isotherm models

	296 K	308 K	323 K	343 K
Freundlich				
K_f (mg/g)	1.855	1.541	1.384	0.997
$1/n$	0.456	0.483	0.492	0.536
R^2	0.969	0.981	0.984	0.989
HYBRID	8.541	6.407	4.930	3.096
Langmuir				
Q_o	15.207	15.419	15.066	14.515
a_L	0.061	0.047	0.041	0.030
R^2	0.993	0.992	0.994	0.994
HYBRID	1.806	2.450	1.880	1.734
Temkin				
K_T	0.826	0.645	0.596	0.429
b	842.174	832.952	873.623	905.686
R^2	0.984	0.955	0.946	0.908
HYBRID	4.563	7.034	8.321	7.237

Table 5
Comparison of three-parameter isotherm models

	296 K	308 K	323 K	343 K
Redlich–Peterson				
K_R	1.230	0.981	0.858	0.629
a_R	0.169	0.155	0.151	0.148
β	0.835	0.808	0.793	0.745
R^2	0.998	0.996	0.998	0.998
HYBRID	0.194	1.180	0.732	0.467
Sips				
q_m	18.163	19.018	19.124	19.670
a_s	0.068	0.053	0.047	0.033
$1/n$	0.822	0.814	0.802	0.800
R^2	0.997	0.996	0.998	0.998
HYBRID	0.405	1.324	0.475	0.561
Khan				
q_m	8.062	7.260	6.737	5.161
b_k	0.140	0.123	0.114	0.108
a_K	0.775	0.735	0.719	0.647
R^2	0.999	0.996	0.997	0.998
HYBRID	0.194	1.166	0.889	0.456

Consideration of all error values reveals that fitting degree of isotherm models were classified as Khan > R–P > Sips > Langmuir > Temkin > Freundlich. These results showed that ammonium exchange by Bigadiç zeolite was characterized by Khan isotherm model and all parameters of Khan isotherm decreased with increasing temperature. Decreasing of parameters with increasing temperature indicated that ammonium uptake is an exothermic reaction. This is in well agreement with the results in literature for ammonium exchange with zeolite [24–25]

3.2. Thermodynamic evaluation

The analysis of equilibrium thermodynamic was made for evaluating the chemical behaviour of ammonium removal by Bigadiç clinoptilolite. Since equilibrium data were characterized by Khan isotherm model, the thermodynamic parameters were calculated by the Khan and Sing [26] method. According to this method, K_o was determined by plotting $\ln(q_e/C_e)$ versus q_e and extrapolating to zero q_e (Fig. 3). The thermodynamic

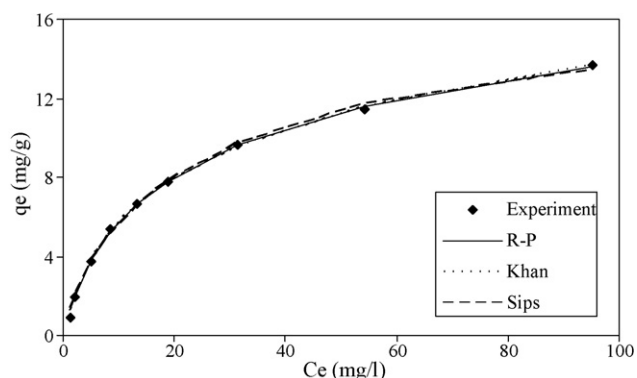


Fig. 2. Comparison of three-parameters isotherm models with experimental data (Temperature: 296 K).

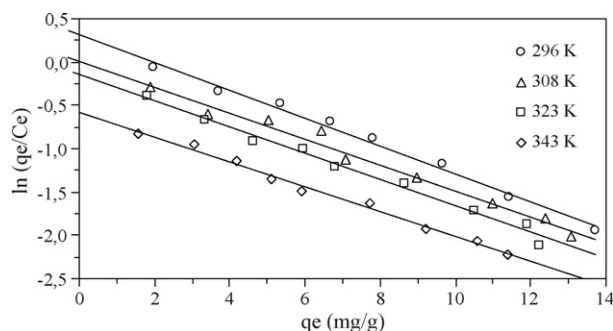


Fig. 3. Calculation of K_o values at various temperatures.

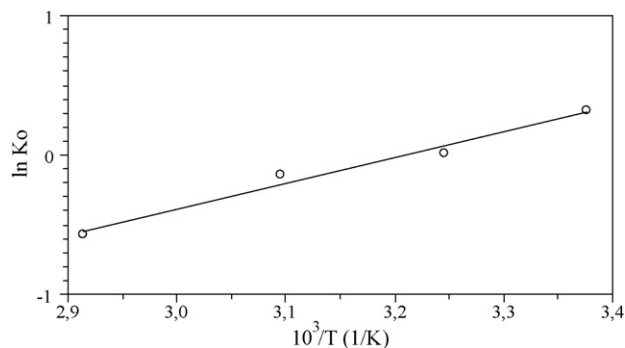


Fig. 4. Plot of $\ln K_o$ vs. $1/T$.

parameters such as change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated using K_o values as described in Eq. (14). The values of ΔH° and ΔS° were determined from the slope and intercept of the Fig. 4 which is plotted using Eq. (15).

$$\Delta G^\circ = -RT \ln K_o \quad (14)$$

$$\ln K_o = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (15)$$

As it is seen in Table 6, ΔG° values at 296 and 308 K are negatives at 296 and 308 but positive at 323 and 343 K. The negative values of ΔG° indicate that ammonium exchange by Bigadiç clinoptilolite is spontaneous at lower temperatures and the increasing of temperature caused the decreasing of feasibility of ammonium uptake. Similar thermodynamic values for ammonium removal by clinoptilolite was found in literature [2]. The negative value of ΔH° is indicating the exothermic nature of ammonium exchange process [25] which supported is by the decreasing of Khan isotherm parameters with increasing temperature. The negative value of ΔG° reveals the decreased randomness at the solid–solution interface during ammonium removal [27].

Table 6
Thermodynamic parameters of ammonium removal

Temperature (K)	K_o	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
296	1.38	-0.79		
308	1.01	-0.04	-15.38	-49.34
323	0.87	0.39		
343	0.56	1.63		

4. Conclusions

In this study, the equilibrium data of ammonium exchange onto Bigadiç clinoptilolite were modeled using nonlinear regression analysis. Comparison of six isotherm models was made using five error functions and standard normalization error procedure was used to select the best error function. HYBRID function provided the lowest SNE values and was used to obtain isotherm parameters. Three-parameters isotherm models resulted better performance than two-parameters model and order of fitting degree of isotherm models were obtained as Khan > R–P > Sips > Langmuir > Temkin > Freundlich. The effect of temperature on the ammonium removal was investigated and the thermodynamic parameters were calculated. Thermodynamic investigation showed that ammonium uptake by clinoptilolite was easier at lower temperatures.

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