

Adsorption characteristics of ammonium ion by zeolite 13X

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Abstract

With synthetic wastewater, lab-scale batch experiments and column experiments were carried out to investigate the adsorption characteristics of ammonium ion by zeolite 13X which is a hydrothermally synthetic byproduct accompanied with preparation of potassium carbonate from insoluble potash ores. The Langmuir and Freundlich models were applied to describe the equilibrium isotherms for ammonium ion uptake and the Langmuir model agrees very well with experimental data. Thermodynamic parameters including changes in the standard free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were also calculated. The results show that the exchange process of ammonium ion by zeolite 13X is spontaneous and exothermic. The pseudo second-order kinetic model was found to provide excellent kinetic data fitting ($R^2 > 0.999$). The effects of relevant dynamic parameters, such as influent flow rate, adsorbent bed height and initial ammonium ion concentration on the adsorption of ammonium ion were examined, respectively. The Thomas model was applied to predict the breakthrough curves and to determine the characteristic parameters of column useful for process design and was found suitable for describing the adsorption process of the dynamic behavior of the zeolite 13X column. The total adsorbed quantities, equilibrium uptakes and total removal percents of ammonium ion related to the effluent volumes were determined by evaluating the breakthrough curves obtained at different conditions.

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1. Introduction

Nitrogen pollution in hydrosphere has recently attracted increasing attention for eutrophication of lakes and rivers all over the world. Ammonium is the inorganic ion form of nitrogen pollution contained in municipal sewage, industrial wastewater and agricultural wastes or decomposed from organic nitrogen compounds in those wastewater and wastes. Higher concentration of ammonium will cause a sharp decrease of dissolved oxygen and obvious toxicity on aquatic organisms [1]. Hence, removing ammonium from wastewater is of great importance to control nitrogen pollution. A variety of biological and physicochemical methods and technologies have been proposed for the removal of ammonium ion from the environ-

ment and industrial water systems [2]. The traditional method for ammonium removal from municipal and industrial wastewaters is based on biological treatments. Since biological methods (nitrification–denitrification) do not respond well to shock loads of ammonium, unacceptable peaks may appear in the effluent ammonium concentration. With the adoption of stringent nitrogen discharge limit of wastewater, ion exchange and adsorption become more interesting as possible treatment methods. Zeolites are aluminosilicate minerals containing exchangeable alkali or alkaline-earth metal cations (normally Na, K, Ca, and Mg) as well as water in their structural framework of zeolite. Their physical structure is porous, and alkali or alkaline-earth cations reversibly fixed in the cavities can easily be exchanged by surrounding positive ions [3]. In recent years, different forms of natural zeolite have been tested to remove ammonium from secondary effluent or sewage [4–6] as well as from industrial wastewater, such as aquaculture wastewater [7] and piggery waster [8,9]. Ion exchange kinetics and equilibrium isotherms were studied using batch experiment technique [10,11].

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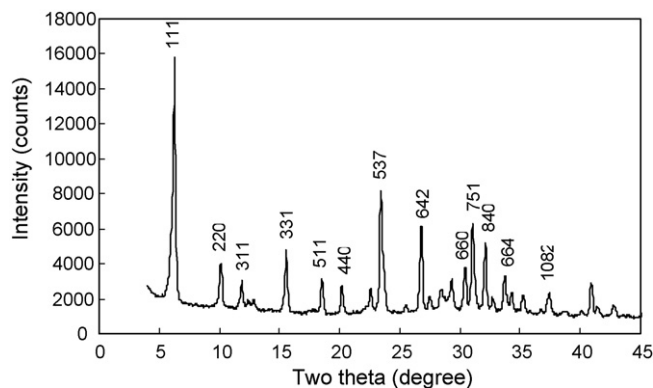


Fig. 1. XRD pattern of the zeolite 13X.

In this study, zeolite 13X, a byproduct obtained from preparation of potassium carbonate from insoluble potash ores by hydrothermal synthesis, was chosen as adsorbent of ammonium ion. The zeolite has been studied as adsorbents of heavy metal ions [12–14] and low concentration ammonium ion [15], and the satisfactory adsorption capacities were obtained. The adsorption characteristics of ammonium ion with medium concentration including ion exchange isotherms, thermodynamic parameters, kinetic models and dynamic parameters by zeolite 13X were not reported. The adsorption characteristics are important to predict the adsorption process and to determine the characteristic parameters of column useful for process design.

2. Materials and methods

Zeolite 13X is a hydrothermally synthetic byproduct from preparation of potassium carbonate using potassium feldspar power with cation exchange capacity of 214.56 cmol/kg. Potassium feldspar power used in this investigation was obtained from Sha County, Fujian Province, China, and is comprised of 67.38% of SiO₂, 16.21% of Al₂O₃, 9.75% of K₂O, 2.35% of Na₂O, 1.07% of CaO, 0.96% of MgO, 0.53% of Fe₂O₃, 0.61% of FeO, 0.04% of MnO, 0.09% of TiO₂ and 0.17% of P₂O₅. Zeolite 13X was prepared using following method [16]: a complete mixing of potassium feldspar power and Na₂CO₃ according to molar ratio of 1.3:1, and baked for 150 min at 845 °C. The product according to molar ratio of M₂O/SiO₂ of 1.5:1 and molar ratio of H₂O/M₂O of 40:1 was added to hydrothermally synthetic reactor in a water bath. Hydrothermally synthetic temperatures of 95–100 °C, synthetic time of 8 h, and the volume of crystal seed of 9.0% were chosen. Excessive base was removed by deionised water washings until pH value of the solution was 9–10. The sample prepared was dried in an oven at 105 °C for 10 h. XRD pattern of the zeolite 13X was shown in Fig. 1 and the chemical compositions were summarized in Table 1.

Analytical grade ammonium chloride salt (NH₄Cl) and deionised water were used in the preparation of the stock NH₄⁺ solutions. The stock solutions were diluted to prepare for working solutions by using deionised water. The initial pH value was adjusted by addition of NaOH or HCl to designed value.

The batch experiments were initiated by a complete mixing of 50 mL synthetic wastewater in the range of 5–400 mg/L initial

Table 1
Chemical compositions of zeolite 13X

Constituent	Value (wt.%)
SiO ₂	43.87
Al ₂ O ₃	25.67
TiO ₂	0.13
Fe ₂ O ₃	1.80
FeO	0.21
MnO	0.45
MgO	1.04
CaO	2.05
Na ₂ O	9.56
K ₂ O	3.38
P ₂ O ₅	0.22
H ₂ O	11.62

NH₄⁺ concentration with pH value of about 7.0 and 0.8 g of zeolite 13X samples that were crushed and sieved using 200-mesh (75 μm) sieve in a serial of 100 mL plug-contained conical flasks. Then, the bottles were shaken in HZQ-C air bath and constant temperature oscillator at a speed of 140 rounds per min at a room temperature of 25 ± 0.5 °C except the experiment of the effect of temperature. Water samples in conical flasks were filtrated rapidly with 0.45 μm membranes at 30 min except the dynamic experiments at frequent intervals, and the filtrates were used immediately to analyze the concentration of NH₄⁺. The removal efficiency (%) and amounts of exchanged NH₄⁺ ion (*q_e*) by the zeolite were calculated using Eqs. (1) and (2), respectively:

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where *V* is the solution volume (L), and *m* is the adsorbent weight (g).

Column experiments were performed in an organic glass column with a diameter of 6.0 cm, and length of 50 cm. The column was naturally packed with 500 g of zeolite 13X with an average particle diameter of 4–6 mm to reach a bed height of 21.4 cm. During the experiment of the effect by bed height, the mass of 13X zeolite in the column was 25, 500 and 900 g, respectively. The influent with initial NH₄⁺ concentration of 80 mg/L down-flow passed the fixed-bed with a valve from the top of the column at a specified flow rate. Effluents were collected at regular intervals and the concentration of the ammonium ion in the effluent was analyzed immediately. In this paper, breakthrough and exhaustion were defined as the phenomenon when effluent concentration met Chinese first-level discharge standard of industrial wastewater about ammonium ion and effluent concentration was about 95% of initial concentration.

The concentration of the ammonium ion was analyzed using ammonium ion selective electrode.

3. Results and discussion

3.1. Ammonium ion exchange isotherms

Usually, Langmuir and Freundlich models are used to describe the equilibrium isotherm data.

The linear form of Langmuir model is expressed as the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_0} C_e + \frac{1}{q_0 k} \tag{3}$$

where q_e is the equilibrium amount of adsorbate adsorbed (mg) by per unit mass of adsorbent (g), C_e is the concentration of adsorbate in equilibrium solution (mg/L), and the values of q_0 (mg/g) and k (L/mg) are maximum adsorption capacity of adsorbent and the adsorption energy coefficient, respectively.

The essential features of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor R_L :

$$R_L = \frac{1}{1 + kC_0} \tag{4}$$

where C_0 (mg/L) is initial concentration of adsorbate and k is the Langmuir constant (L/mg). There are four probabilities for the R_L value: for favorable adsorption, $0 < R_L < 1$; for unfavorable adsorption, $R_L > 1$; for linear adsorption, $R_L = 1$; for irreversible adsorption, $R_L = 0$ [11,17,18].

The linear form of Freundlich model is expressed as follows:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{5}$$

where K_f is Freundlich constant (mg/g), the measure of the adsorption capacity of the adsorbent, and $1/n$ is the heterogeneity factor, a constant relating to adsorption intensity or surface heterogeneity.

Linear plot of Langmuir isotherm of NH_4^+ ion adsorption on zeolite 13X was shown in Fig. 2. The correlation coefficient value of the linear plot was found satisfactory ($R^2 = 0.9957$). The maximum adsorption capacity of adsorbent (q_0) and the adsorption energy coefficient (k) calculated from the slope and the intercept of the linear plot were 8.61 mg/g and 0.044 L/mg at

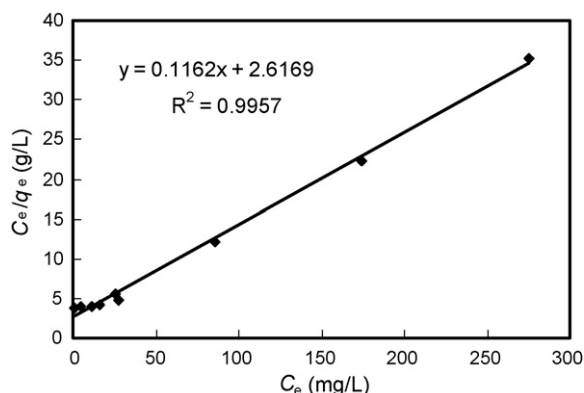


Fig. 2. Linear plot of Langmuir isotherm of NH_4^+ ion adsorption on zeolite 13X.

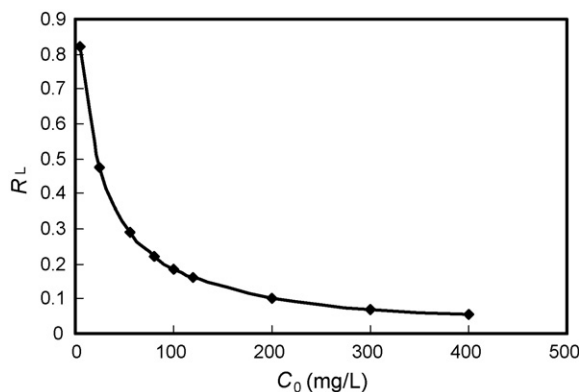


Fig. 3. Variation of separation factor (R_L) as a function of initial NH_4^+ ion concentration.

25 °C, respectively. Lebedynets et al. [19] and Karadag et al. [10] reported that the maximum amounts of exchanged NH_4^+ using the transcarpathian clinoptilolite and natural Turkish clinoptilolite were 11.5 and 8.121 mg/g at 25 °C, respectively. Weatherley and Miladinovic [20] found the maximum amounts of exchanged NH_4^+ by New Zealand clinoptilolite and mordenite to be 6.588 and 9.479 mg/g, respectively. Saltali et al. reported that the maximum amount of exchanged NH_4^+ by natural Turkish (Yıldızeli) zeolite was 9.64 mg/g at 21 °C [11].

Fig. 3 shows the variation of separation factor (R_L) with initial NH_4^+ ion concentration. The results that the R_L values were in the range of 0–1 indicate that the exchange of NH_4^+ ion by zeolite 13X is favorable. That the R_L value approaches zero with the increase of C_0 means that the adsorption of NH_4^+ ion onto zeolite 13X is less favorable at high initial NH_4^+ ion concentration.

Linear plot of Freundlich isotherm of NH_4^+ ion adsorption on zeolite 13X was shown in Fig. 4. Compared with the correlation coefficient value of the linear plot of Langmuir isotherm, that of Freundlich model was found less satisfactory ($R^2 = 0.859$). We can note that the Freundlich isotherm is not thermodynamically consistent as it does not reduce to Henry’s law in the limit of infinite dilution. As such, design based on Freundlich isotherm is less satisfactory when the process demands nearly complete removal of ammonium ion. Freundlich constant (K_f) and the heterogeneity factor ($1/n$) calculated from the slope and the intercept of the linear plot were 0.50 mg/g and 0.589, respec-

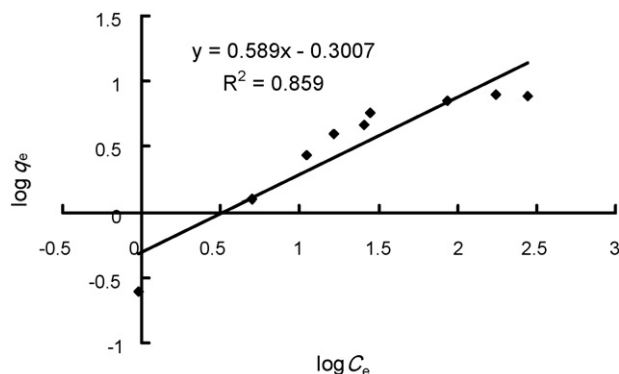


Fig. 4. Linear plot of Freundlich isotherm of NH_4^+ ion adsorption on zeolite 13X.

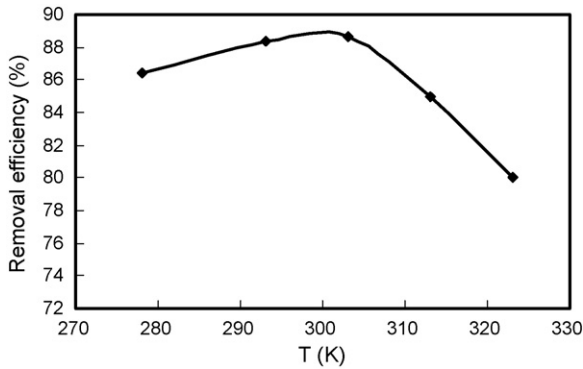


Fig. 5. Effect of temperature on NH_4^+ ion removal using zeolite 13X (initial NH_4^+ ion concentration: 80 mg/L).

tively. The value of $1/n$ smaller than 1 pointed out the favorable removal conditions [9,10].

3.2. Thermodynamic parameters

The effect of temperature on NH_4^+ ion removal on zeolite 13X was found to be complicated (as shown in Fig. 5). Removal efficiency of NH_4^+ ion increases with the increase of temperature when temperature is lower than room temperature (about 25 °C) and removal efficiency of NH_4^+ ion decreases with the increase of temperature when temperature is higher than room temperature. The possible reason is attributed to the existence of chemical adsorption during the adsorption process. Adsorption rate is slow in the process of chemical adsorption and higher temperature is favorable to improving the adsorption rate. However, higher temperature is unfavorable to exothermic reaction once equilibrium is attained. Therefore, there is a tendency for the ammonium ion to desorb from the solid phase to the bulk phase with an increase in the temperature of the solution [10].

The amount of NH_4^+ exchanged at equilibrium at different temperatures of 30, 40 and 50 °C was used to calculate and obtain thermodynamic parameters. Thermodynamic parameters such as changes in the standard free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were calculated using following equations:

$$K_C = \frac{C_{Ae}}{C_{Se}} \quad (6)$$

$$\Delta G^0 = -RT \ln K_C \quad (7)$$

$$\ln K_C = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (8)$$

where K_C is the equilibrium constant, C_{Ae} is the amount of adsorbate on the adsorbent per L of the solution at equilibrium (mg/L), C_{Se} the equilibrium concentration of adsorbate in the solution (mg/L). T is the solution temperature (K) and R is the gas constant and is equal to 8.314 J/mol K.

ΔH^0 and ΔS^0 were calculated from the slope and intercept of linear plot of $1/T$ versus $\ln K_C$ (as shown in Fig. 6). The values of K_C , ΔG^0 , ΔH^0 and ΔS^0 parameters were summarized in Table 2.

Change in the standard free energy ΔG^0 with negative values for -5.18 , -4.51 and -3.72 kJ/mol at all the experimental temperature indicates that ammonium exchange by zeolite 13X

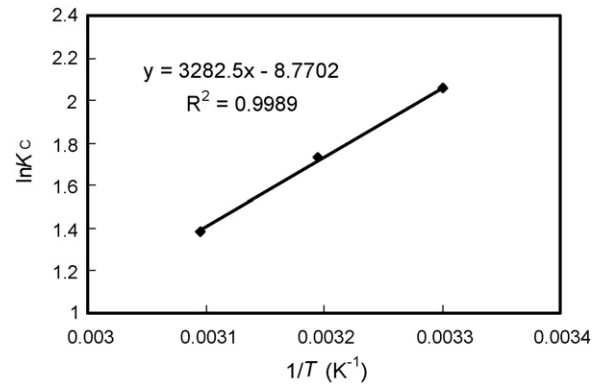


Fig. 6. Variation of equilibrium constant (K_C) as a function of temperature (initial NH_4^+ ion concentration: 80 mg/L).

is spontaneous. Furthermore, ammonium exchange has physical characteristics since the free energy change is between 0 and -20 kJ/mol [21].

Change in the standard enthalpy ΔH^0 has a value of -27.29 kJ/mol. The negative ΔH^0 exhibits that the NH_4^+ ion exchange by zeolite 13X is exothermic. The negative value of the standard entropy change ΔS^0 (-72.92 J/K mol) indicates that the randomness decreases with the removal of NH_4^+ on zeolite 13X.

3.3. Kinetics of ammonium ion exchange

Pseudo second-order model was used for analysis of ammonium ion exchange kinetics. Pseudo second-order model is represented as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (9)$$

where q_t is the amount of adsorbate exchanged (mg/g) at time t , k_2 is the rate constant (g/mg min).

Pseudo second-order kinetic plot for NH_4^+ ion exchange by zeolite 13X at 25 °C was shown in Fig. 7. The higher correlation coefficient value ($R^2 > 0.999$) indicates that the ammonium ion uptake by zeolite 13X follows pseudo second-order model. The result is accordant with that reported about natural Turkish clinoptilolite [10]. Based on Eq. (9), values of k_2 and q_e were obtained from the straight-line plot of t/q_t against t and were 0.79 g/mg min and 4.43 mg/g, respectively.

Table 2
Change of thermodynamic parameters with temperature

Temperature (°C)	K_C	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/K mol)
30	7.82	-5.18	-27.29	-72.92
40	5.65	-4.51		
50	4.00	-3.72		

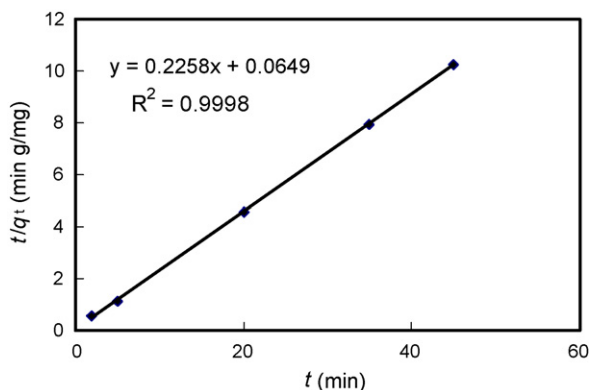


Fig. 7. Pseudo second-order kinetic plot for NH_4^+ ion exchange by zeolite 13X (initial NH_4^+ ion concentration: 80 mg/L).

3.4. Effect of bed height on the performance of breakthrough and application of Thomas model

The loading behavior of adsorbate to be removed from aqueous solution in a fixed-bed is usually expressed in terms of C/C_0 (C = effluent adsorbate concentration and C_0 = influent adsorbate concentration) as a function of volume or time of the eluate for a given bed height, giving a breakthrough curve [22]. The maximum column capacity, q_{total} (mg), for a given feed concentration and flow rate is equal to the area under the plot of the adsorbed adsorbate concentration C_{ad} ($C_{\text{ad}} = C_0 - C$) (mg/L) versus volume (L) and is calculated from Eq. (10):

$$q_{\text{total}} = \int_{V=0}^{V=V_{\text{total}}} c_{\text{ad}} dV \quad (10)$$

The equilibrium uptake ($q_{\text{eq(exp)}}$), the weight of adsorbate adsorbed per unit dry weight of adsorbent (mg/g) in the column, is calculated as follows:

$$q_{\text{eq(exp)}} = \frac{q_{\text{total}}}{X} \quad (11)$$

where X is the total dry weight of adsorbent in column (g).

Total amount of adsorbate sent to column (W_{total}) is calculated from Eq. (12):

$$W_{\text{total}} = C_0 V_{\text{total}} \quad (12)$$

Total removal percent (Y) of adsorbate is the ratio of the maximum capacity of the column (q_{total}) to the total amount of adsorbate sent to column (W_{total}).

$$Y = \frac{q_{\text{total}}}{W_{\text{total}}} \times 100 \quad (13)$$

Successful design of a column adsorption process requires prediction of the concentration–effluent volume profile or breakthrough curve for the effluent. The maximum adsorptive quantity of an adsorbent is needed in design. The Thomas equation is widely used to predict heterogeneous ion exchange in a flowing system [23,24]. The Thomas equation can be expressed as follows:

$$\frac{C}{C_0} = \frac{1}{1 + \exp[k_{\text{Th}}/Q(q_0X - C_0V_{\text{eff}})]} \quad (14)$$

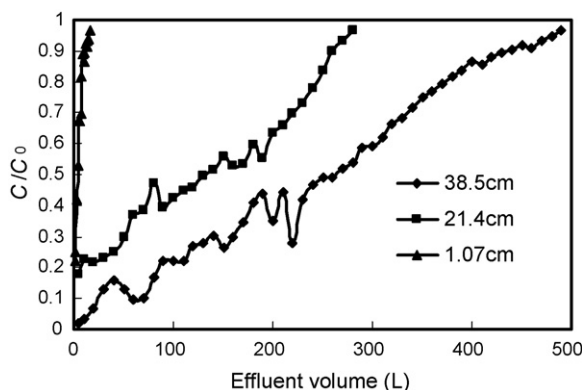


Fig. 8. Effect of bed height on breakthrough curves for adsorption of ammonium ion by zeolite 13X (flow rate = 119.43 mL/min, C_0 = 80 mg/L, pH 5.23).

where K_{Th} is the Thomas rate constant (mL/min mg); q_0 is the maximum solid-phase concentration of solute (mg/g). X is the amount of adsorbent in the column (g); V_{eff} is the effluent volume (L); Q is the flow rate (mL/min).

The linearized form of the Thomas model is as follows:

$$\ln\left(\frac{C_0}{C} - 1\right) = \frac{k_{\text{Th}}q_0X}{Q} - \frac{k_{\text{Th}}C_0}{Q}V_{\text{eff}} \quad (15)$$

The kinetic coefficient K_{Th} and the adsorption capacity of the column q_0 can be determined from a plot of $\ln(C_0/C - 1)$ against V_{eff} at a given flow rate.

The breakthrough curves of ammonium ion adsorption obtained at different bed heights with a constant flow rate of 119.43 mL/min were given in Fig. 8. The bed heights of column were approximately 1.07, 21.4 and 38.5 cm, corresponding to 25, 500, 900 g of zeolite 13X. The feed concentration with a synthetic solution contained 80 mg/L ammonium ion. The breakthrough curves in Fig. 8 show that adsorbent bed height strongly affects the volume of solution treated or throughput volume. The volume of solution treated increases with the increase in bed height and the slope of the plots from breakthrough volume to exhaustion volume decreases as the bed height increased from 1.07 to 38.5 cm, indicating the breakthrough curve becomes steeper as the bed height decreases. It is illustrated that the higher the bed height the more the volume of solution treated at various breakthroughs due to the increase in exchangeable cation ions in the adsorbent.

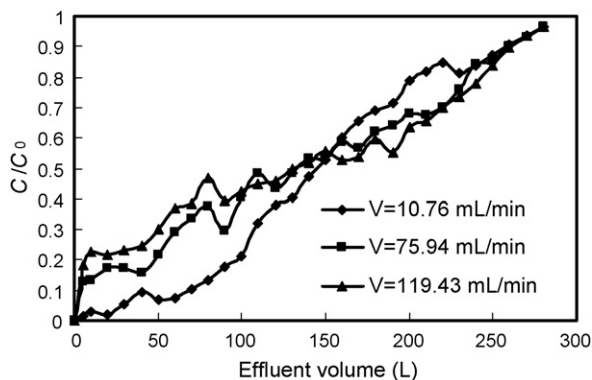
To determine the maximum solid-phase concentration (q_0) and Thomas rate constant K_{Th} at different bed height in column, the data were fitted to the Thomas equation model by using linear regression analysis. A plot of $\ln(C_0/C_e - 1)$ versus V_{eff} gives a straight line with a slope of $(K_{\text{Th}}C_0/Q)$ and an intercept of $(K_{\text{Th}}q_0X/Q)$. Therefore, the values of equation parameters such as K_{Th} and q_0 when application of Thomas model to the data at C/C_0 ratios higher than 0.02 and lower than 0.95 with respect to different bed height can be obtained. The relative parameters were listed in Table 3.

As shown in Table 3, the removal efficiency of ammonium ion increases with an increase in bed height, and results also show higher equilibrium capacities ($q_{\text{eq(exp)}}$) of the three bed heights with values from 15.74 to 24.20 mg/g. It can also be seen that the

Table 3

Parameters predicted from the Thomas model of ammonium ion adsorption at different bed height (flow rate = 119.43 mL/min, $C_0 = 80$ mg/L, pH 5.23)

Bed height (cm)	W_{total} (mg)	q_{total} (mg)	Y (%)	$q_{\text{eq(exp)}}$ (mg/g)	$q_{0(\text{cal})}$ (mg/g)	K_{Th} (mL/min mg)	R^2
1.07	1280	393.5	30.74	15.74	12.63	0.424	0.9452
21.4	22400	10585	47.25	21.17	19.90	0.019	0.8812
38.5	39200	21780	55.56	24.20	21.68	0.017	0.9616

Fig. 9. Effect of flow rate on breakthrough curves for adsorption of ammonium ion on zeolite 13X ($C_0 = 80$ mg/L, pH 5.23, bed height = 21.4 cm).

values of K_{Th} decrease with increasing of the bed height. Inspection of each line indicates that they all fit with linear correlation coefficients (R^2) ranging from 0.8812 to 0.9616. With the higher value of R^2 , it can be said that the Thomas model equations of linear regression analysis could describe the breakthrough data under the studied conditions. The maximum adsorption capacities ($q_{0(\text{cal})}$) of ammonium ion predicted by the model were found to be affected by bed height, and the values of $q_{0(\text{cal})}$ estimated by this model differed insignificant of those measured experimentally. So, it is also indicated that the Thomas model gives well-fit experimental data under this study conditions. The results are accordant with those reported about copper(II) and lead(II) removal from aqueous solution in fixed-bed columns by manganese oxide coated zeolite [24].

3.5. Effect of flow rate on the performance of breakthrough and application of Thomas model

To investigate the effect of flow rate on adsorption of ammonium ion by zeolite 13X, the inlet ammonium ion concentration in the feed was held constant at 80 mg/L. The flow rate was from 10.76 to 119.43 mL/min at a bed height of 21.4 cm. Effect of flow rate on breakthrough curves for adsorption of ammonium ion on zeolite 13X was presented in Fig. 9.

It is illustrated that the breakthrough volume reaching Chinese first-level discharge standard of industrial wastewater

($C = 15$ mg/L, $C/C_0 = 0.19$) about ammonium ion increases significantly (from 6 to 92 L) with a decrease of flow rate from 119.43 to 10.76 mL/min and the breakthrough curves shifts from left to right before effluent reaches 150 L. But the breakthrough curves differ insignificantly from each other after 150 L.

The relative parameters such as q_0 and K_{Th} at different flow rate in column modeled by the linearized form of the Thomas model were listed in Table 4. As shown in Table 4, the removal efficiency of ammonium ion decreases with an increase in flow rate, and results also show higher equilibrium capacities ($q_{\text{eq(exp)}}$) of the three flow rate with values from 21.17 to 23.77 mg/g. It can also be seen that the values of K_{Th} increase with increasing of the flow rate. The inspection of each line indicates that they all fit with linear regressive coefficients (R^2) ranging from 0.8812 to 0.9821. With the higher value of R^2 , it can be said that the Thomas model equations of linear regression analysis could describe the breakthrough data under the studied conditions. The maximum adsorption capacities ($q_{0(\text{cal})}$) of ammonium ion predicted by the model were found to be affected by flow rate, and the values of $q_{0(\text{cal})}$ estimated by this model differed insignificant of those measured experimentally. So, it is also indicated that the Thomas model gives well-fit experimental data under this study conditions. The results are also accordant with those reported about copper(II) and lead(II) removal from aqueous solution in fixed-bed columns by manganese oxide coated zeolite [24].

3.6. Effect of initial concentration of ammonium ion on the performance of breakthrough and application of Thomas model

The effect of initial influent concentration was investigated using synthetic solution containing 30, 80, 200 mg/L of ammonium ion. Fig. 10 shows the effect of initial concentration on the breakthrough curves by using a bed height of 21.4 cm at a flow rate of 75.94 mL/min. As shown from the breakthrough curves in Fig. 10, the initial concentration of ammonium ion strongly affects the volume of solution treated or exhaustion volume. The volume of solution treated increases with the decrease in initial concentration and the slope of the plots from throughput volume increases as the initial concentration increases from 30 to

Table 4

Parameters predicted from the Thomas model of ammonium ion adsorption at different flow rates ($C_0 = 80$ mg/L, pH 5.23, bed height = 21.4 cm)

V (mL/min)	W_{total} (mg)	q_{total} (mg)	Y (%)	$q_{\text{eq(exp)}}$ (mg/g)	$q_{0(\text{cal})}$ (mg/g)	K_{Th} (mL/min mg)	R^2
10.76	22400	11885	53.06	23.77	24.59	0.003	0.9821
75.94	22400	11020	49.20	22.04	21.23	0.015	0.9460
119.43	22400	10585	47.25	21.17	19.90	0.019	0.8812

Table 5

Parameters predicted from the Thomas model of ammonium ion adsorption at different initial concentrations ($V = 75.94$ mL/min, pH 5.23, bed height = 21.4 cm)

C_0 (mg/L)	W_{total} (mg)	q_{total} (mg)	Y (%)	$q_{\text{eq(exp)}}$ (mg/g)	$q_{0(\text{cal})}$ (mg/g)	K_{Th} (mL/min mg)	R^2
30	15600	8935	57.28	17.87	18.46	0.017	0.8424
80	22400	11020	49.20	22.04	21.23	0.015	0.9460
200	36000	11395	31.65	22.79	17.10	0.008	0.9637

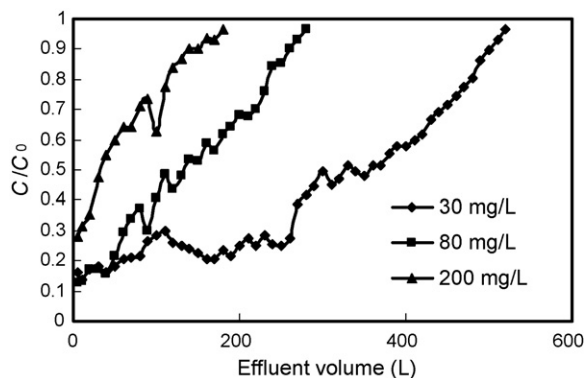


Fig. 10. Effect of initial concentration on breakthrough curves for adsorption of ammonium ion on zeolite 13X ($V = 75.94$ mL/min, pH 5.23, bed height = 21.4 cm).

200 mg/L, indicating the breakthrough curve becomes steeper as the initial concentration increases. It is illustrated that the lower the initial concentration is, the more the volume of solution treated is at various breakthroughs due to the same exchangeable cation ions in the adsorbent.

According to linearized Thomas equation, the q_0 , K_{Th} and correlation coefficients R^2 were calculated and were shown in Table 5. The removal efficiency of ammonium ion decreases with an increase in initial concentration, and results also show higher equilibrium capacities ($q_{\text{eq(exp)}}$) of the three initial concentration with values from 17.87 to 22.79 mg/g. It can also be seen that the values of K_{Th} decrease with increase of the initial concentration. Inspection of each line indicates that they all fit with linear correlation coefficients (R^2) ranging from 0.8424 to 0.9637. With the higher value of R^2 , it can be said that the Thomas model equations of linear regression analysis could describe the breakthrough data under the studied conditions. The maximum adsorption capacities ($q_{0(\text{cal})}$) of ammonium ion predicted by the model were found to be affected by initial concentration, and the values of $q_{0(\text{cal})}$ estimated by this model differed insignificant of those measured experimentally. So, it is also indicated that the Thomas model gives well-fit experimental data under this study conditions. Similarly, the results are also accordant with those reported about copper(II) and lead(II) removal from aqueous solution in fixed-bed columns by manganese oxide coated zeolite [24].

4. Conclusions

- (1) The NH_4^+ ion exchange data on zeolite 13X fitted better to Langmuir model ($R^2 = 0.9957$) than Freundlich model ($R^2 = 0.859$). R_L value from Langmuir isotherm and $1/n$

from Freundlich isotherm indicate that the removal of NH_4^+ ion on zeolite 13X is favorable.

- (2) The negative values of ΔG^0 at the experimental temperatures of 30, 40 and 50 °C indicate that ammonium exchange by zeolite 13X is spontaneous. The negative values of ΔH^0 and ΔS^0 exhibit that the NH_4^+ ion exchange by zeolite 13X is exothermic and the randomness decreases with the removal of NH_4^+ on zeolite 13X.
- (3) The pseudo second-order kinetic model agrees very well with the dynamic data for the exchange of NH_4^+ ion on zeolite 13X.
- (4) The Thomas mathematical model adequately described the adsorption of ammonium ion on zeolite 13X by column mode.

The results indicate that there is a significant potential for the zeolite 13X as an adsorbent material for ammonium removal from aqueous solutions.

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