

Removal of ammonium from wastewater using calcium form clinoptilolite

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Received 16 January 2006; received in revised form 5 June 2006; accepted 8 July 2006

Available online 14 July 2006

Abstract

The paper concerns the removal of ammonium ions from aqueous solution using a modified clinoptilolite—Ca²⁺-formed clinoptilolite (CaY) prepared from natural clinoptilolite. The batch study results show that the pH has an effect on ammonium adsorption capacity as it can influence both the character of the exchanging ions and the clinoptilolite itself; the CaY has a high selectivity to NH₄⁺ and the exchange decreases with increasing temperature; ammonium ion uptake onto CaY was suitably described by the Langmuir model. The column results indicated that the effluent of simulated wastewater treated with CaY could meet the integrated wastewater discharge standard of China, and CaY can be circulated through regenerating by Ca(OH)₂.

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Keywords: Ammonium removal; Clinoptilolite; Wastewater; Thermodynamics

1. Introduction

Nitrogen compounds are very essential elements for living organisms. However, when they are more than needed, they can contribute to accelerated eutrophication of lakes and rivers, dissolved oxygen depletion and fish toxicity in receiving water. Ammonia is usually found as ammonium ion (NH₄⁺) in aqueous environments. The common ammonium removal processes are air stripping, chemical treatment, selective ion exchange and biological nitrification–denitrification [1–3]. An attractive process for removal of ammonium is ion exchange [4–9]. The ion exchange method usually employs organic resins, which are selective but very expensive. There are, however, cheap alternative materials, such as natural zeolite, which are abundant in nature.

Natural zeolites are the most important inorganic cation exchangers that exhibit high ion exchange capacity, selectivity and compatibility with the natural environment [10]. In the

last 20 years, characteristics of natural zeolites have been intensively studied for the needs of wastewater treatment. Clinoptilolite, which has a high affinity for ammonium ion, is one of the most important natural zeolites because it is found in large deposits worldwide. Clinoptilolite is reported to have a classical alumina silicate age-like structure and exhibits significant macro-porosity. It is very stable towards dehydration and its thermal stability, 700 °C in air, is considerably greater than the stability of other natural zeolites with similar structure [11–13].

Among natural zeolites, clinoptilolite occurs most frequently, e.g. in USA, Russia and Hungary. China is also rich in clinoptilolite reserves [14]. Mercer had suggested the use of clinoptilolite whose calcium and sodium forms are highly selective for ammonium ions [15]. So far, most researches focused on Na⁺-formed clinoptilolite (NaY) for ammonia removal and generally approved NaY as the most suitable form. But studies on Ca²⁺-formed clinoptilolite (CaY) are rarity.

It is another distinction that clinoptilolite could be utilized time after time through regeneration. Generally, the desorption and regeneration of NaY having adsorbed NH₄⁺ can be achieved in two approaches: one is to use saturated NaCl solution at pH 11–12 adjusted by using NaOH [16,17], the

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other is to use $\text{Ca}(\text{OH})_2$ latex origin in a mixture of calces and water [1] followed by saturated NaCl solution [14]. The latter is obviously cost-effective, since the price of $\text{Ca}(\text{OH})_2$ is cheap relative to NaOH. However, few researchers paid close attention to this regeneration method because it needs saturated NaCl solution after eluting the NaY by $\text{Ca}(\text{OH})_2$. If the ion exchange and adsorptive capacity of CaY was close to NaY, and CaY was utilized to removal ammonium, $\text{Ca}(\text{OH})_2$ should be enough to desorption and regeneration, and then the craft be simplified and the charge be cut down.

The aim of this study is to prepare CaY, to explore its ion exchange and adsorption capacities, and determine the practical and effective regenerative conditions of this kind of clinoptilolite for reuse. Further study investigates its performance in ammonium removal from simulated wastewater.

2. Experimental

2.1. Preparation of CaY

Clinoptilolite samples used in this study were taken from Inner Mongolia Autonomous Region, China. The chemical composition of the clinoptilolite is shown in Table 1. All chemicals used in the study were of analytical grade and mainly purchased from Kewei Chemical Reagent Co. (Tianjin, China). All solutions and dilutions were made using distilled water.

The chosen clinoptilolite was ground and sieved into 0.425–0.970 mm mesh (between 20 and 40 mesh) particle size and then washed twice with distilled water (volume ratio of liquid/solid 3:1) to remove any non-adhesive impurities and small particles. NaY was gained by treating the samples three times with saturated NaCl solution at boiling point for 2 h, and then changed into NH_4^+ -formed clinoptilolite (NH_4Y) by washing it with 1 mol/l NH_4Cl solution for 20 min at room temperature. Finally, CaY was prepared through washing the NH_4Y with $\text{Ca}(\text{OH})_2$ solution at boiling point for 2–3 h.

2.2. Batch experiments

In the batch studies, the effects of pH and temperature on ammonium removal efficiency by CaY were examined by using ammonium chloride solution. Experiments were all performed in a column of 7 mm in diameter and 250 mm height and operated in the downflow mode.

Table 1
Chemical composition of clinoptilolite

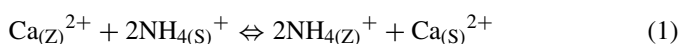
Component	wt. %
SiO_2	68.27 ± 1.23
Al_2O_3	7.48 ± 0.31
Fe_2O_3	1.95 ± 0.20
CaO	2.61 ± 0.15
K_2O	1.69 ± 0.02
Na_2O	0.68 ± 0.03
MgO	1.87 ± 0.15
H_2O	6.26 ± 0.52
Loss on ignition at 1000 °C	7.86 ± 0.36

2.2.1. Effect of pH value

In order to find out the optimum pH value, a 1000 ml of ammonium chloride solution of 300 mg NH_4^+ -N/L was prepared. The solutions were adjusted with hydrochloric acid or calcium hydroxide to pH values ranging from 4 to 9 and were fed into the column system (with approximate 10 g of CaY) at 2 ± 0.2 ml/min. Preliminary tests had confirmed that 2 ± 0.2 ml/min was an optimum flowrate. The outflow was filtrated with a 0.45 μm microporous membrane filter. The samples were analyzed by the standard Nesslerisation method using the 721-spectrophotometer (Shanghai, China) equipped by glass cuvette with an optical way length 1 cm. The maximum exchange capacity of NH_4^+ on the samples was calculated from the margin between the initial and final ammonium concentrations. All the data reported were the average values derived from triplicate samples. Being compared with CaY, the equilibrium uptake of ammonium ion onto NaY was measured at corresponding pH value.

2.2.2. Ion exchange and adsorption isotherms

The ion exchange reaction is a stoichiometric process, where one equivalent of an ion in the solid phase is replaced by equivalent of an ion from solution. The reaction may be written as



The subscripts Z and S refer to the clinoptilolite and solution phase, respectively.

The ion exchange and adsorption isotherms characterize the equilibrium of an ion in solid phase with the concentration of the ion in solution.

The CaY and 0.1 mol/l NH_4Cl solution were placed in a 250 ml flask and shaken in a thermostated shaker for 2 h, which was sufficient for reaching equilibrium. Some experiments were done for different clinoptilolite (g)/solution (ml) ratios. The solid-to-liquid ratio ranged from 1/6 to 1/100. At the designated time the two phases were separated by filtration through a 0.45 μm microporous membrane filter and the solutions were analyzed for ammonium. Three isotherms were obtained at $20(\pm 1)$, $40(\pm 1)$ and $60(\pm 1)$ °C.

In order to determine the performance of CaY, A_s and A_c of NH_4^+ were necessary and they were described by the following equation:

$$A_s = \frac{C_{\text{NH}_4^+}}{C_{\text{NH}_4^+}^0} \quad (2)$$

$$A_c = \frac{V_{\text{NH}_4\text{Cl}}(C_{\text{NH}_4^+} - C_{\text{NH}_4^+}^0)}{mQ} \quad (3)$$

where A_s and A_c are defined as the non-dimensional parameter of NH_4^+ concentration in the aqueous and solid, respectively, $C_{\text{NH}_4^+}$ is the equilibrium NH_4^+ concentration (mmol/l) and $C_{\text{NH}_4^+}^0$ is the initial NH_4^+ concentration in the aqueous phase (mmol/l), $V_{\text{NH}_4\text{Cl}}$ is the volume of NH_4Cl solution (l), m is the mass of clinoptilolite (g) and Q is the maximum exchange capacity of the CaY (mmol/g).

2.2.3. Kielland plots and thermodynamic properties

To obtain the Kielland plots, normalized values of A_c were used as suggested elsewhere [18,19].

The thermodynamic properties were calculated from isotherms data and Kielland plots using the relationship listed below [20,21]:

$$K_c \approx K_t = \frac{A_c^{Z_B}(1 - A_s)^{Z_A}}{(1 - A_c)^{Z_A} A_s^{Z_B}} \quad (4)$$

$$\ln K_a = (Z_B - Z_A) + \int_0^1 \ln K_c dA_c \quad (5)$$

$$\Delta G^\circ = -\frac{RT}{Z_A Z_B} \ln K_a \quad (6)$$

$$\frac{d \ln K_a}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (7)$$

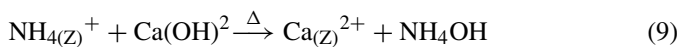
$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \quad (8)$$

where K_c is the Kielland constant, K_a the thermodynamic equilibrium constant, R the universal gas constant (8.314 J/mol K), T the absolute temperature (K), Z_A the charge of NH_4^+ ($Z_A = 1$), Z_B the charge of Ca^{2+} ($Z_B = 2$), ΔG° the free energy (kJ/mol K), ΔH° the standard enthalpy of ion exchange (kJ/mol K) and ΔS° is the standard entropy of reaction (kJ/mol).

The equilibrium isotherms data obtained under known conditions can be used for determining these thermodynamic properties. To determine K_a for the examined exchange processed, the integral on the right-hand side of Eq. (5) was evaluated graphically as the area under the corresponding $\ln K_c$ versus A_c curves, the Kielland plots.

2.3. Desorption and regeneration

A consideration of practical interest with regard to the application of a new exchanger is its desorption and regeneration ability. Clinoptilolite saturated with ammonium ions was regenerated by 0.2 mol/l $\text{Ca}(\text{OH})_2$ emulsion at 100–110 °C, with an ion exchange reaction happened as follows:



This operation went on with generating free ammonia, so some ammoniated by-products (such as NH_4Cl) can be gained.

The mass of the zeolite during the regeneration and the adsorption capacity of the regeneration modified zeolite for ammonium ions after regeneration were measured, respectively.

2.4. Simulated wastewater treatment

In this investigation, column with an inner diameter of 30 mm and height of 5000 mm was used. The volume of the clinoptilolite column was about 320 cm^3 and the mass was about 1440 g. Column was filled with fine zeolite 0.425–0.970 mm. In this

study, some operation parameters and adsorption capacity of zeolite were confirmed.

The simulated wastewater (mainly containing 250 mg/l NH_4Cl , 40 mg/l NaCl , 30 mg/l CaCl_2 , 20 mg/l KCl and 20 mg/l MgCl_2) was fed into the clinoptilolite column system at 10, 40, and 70 ml/min flowrates with constant influent pH of 7. Five liters of samples were taken from the effluent during operation and analyzed for $\text{NH}_4^+\text{-N}$ as previous description.

The column was regeneration with $\text{Ca}(\text{OH})_2$ emulsion at pH 11–12 and at flow velocity of 5 ml/min. Preliminary tests had confirmed that 5 ml/min flowrate was optimum in regeneration process. The regeneration solution was passed through the column in the down mode. Another loading cycle was then carried out when the ammonia in the effluent was absent.

3. Results and discussion

3.1. Adsorption capacity of CaY

The saturated adsorption capacities of CaY and NaY samples for ammonium ions were determined for various pH values, as shown in Fig. 1. Adsorption capacities for CaY determined at pH 4, 5, 6, 7, 8 and 9 were to be 0.6226, 0.7821, 0.8223, 0.7932 and 0.5170 mmol/g, respectively. The values of CaY is little lower than NaY and the maximum adsorption value of CaY and NaY is similarly achieved when operating at pH 6. In addition, the adsorption capacity of CaY for ammonium at pH 5–7 is within the interval of 0.65 mequiv./g (9.15 mg $\text{NH}_4^+\text{-N/g}$) [22], 15 mg/g [23], 25.93 mg/g [13]. Thus, the CaY could be considered as cost effective material for ammonium removal from the wastewater, especially at pH 5–7.

The adsorption capacity for ammonium of clinoptilolite was obviously impacted by pH value of ammonium solution. The reason is that pH can influence both the character of the exchanging ions and the character of the clinoptilolite itself. At lower pH, the ammonium ions have to compete with hydrogen ions among the exchange sites; however, when the pH is higher, the ammonium ions are transformed to aqueous ammonia. On the other hand, a variety of impurities that occupy micropores and macropores of

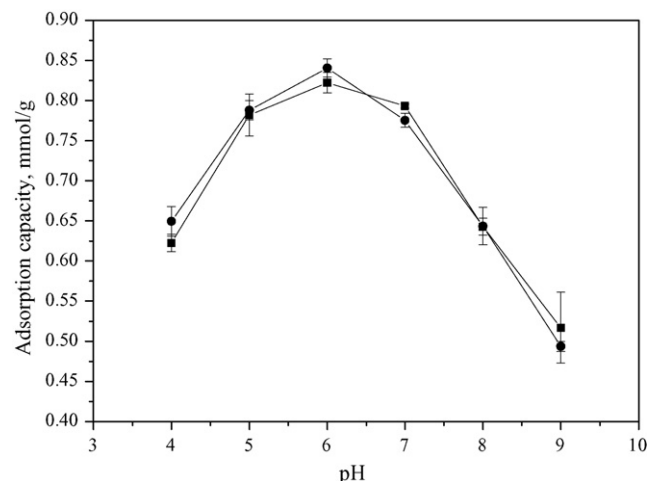


Fig. 1. Adsorption capacity of CaY at different pH values (CaY (■); NaY (●)).

clinoptilolite, such as calcium carbonate, unaltered glass, etc., are perhaps removed by hydrogen ions at lower pH [16]. This might contribute to improving the exchange capacity of clinoptilolite.

3.2. Thermodynamic isotherms of CaY

The direct isotherms for $2\text{NH}_4^+ \rightleftharpoons \text{Ca}^{2+}$ of three temperatures are shown in Fig. 2. One can observe a convexly upward curvature of the isotherms due to the very high preference of CaY for NH_4^+ . Higher temperatures decrease NH_4^+ exchange; however, even at 60°C the ion exchange reaction closes to proceed to completion. It is noted that at 60°C an initial plateau occurred corresponding to A_c near to 0.95. At 40°C , a higher loading ($A_c \approx 0.97$) appeared. And then the values almost reached the maximum value of 1 ($A_c \approx 0.99$) at 20°C .

To check the reproducibility of the data, the equilibrium experiments were repeated three times. The deviations in the values of equivalent fraction in solution and in clinoptilolite were about 0.064. Arithmetic average of the repeated experiments was used for drawing the isotherms and for thermodynamic analysis.

In addition, the mathematical model about thermodynamic equilibrium of Langmuir can be regressed from the data by the least square method at different temperature. The results can be explained as follows:

$$A_c = \frac{aA_s}{1 + bA_s} \quad (11)$$

where the values of a and b were shown in Table 2.

Table 2 presents the results of the regression analysis for Langmuir isotherm model for CaY at three temperatures considered in this research. It can be seen that a very good fit to Langmuir isotherm model ($r^2 > 0.97$) was achieved.

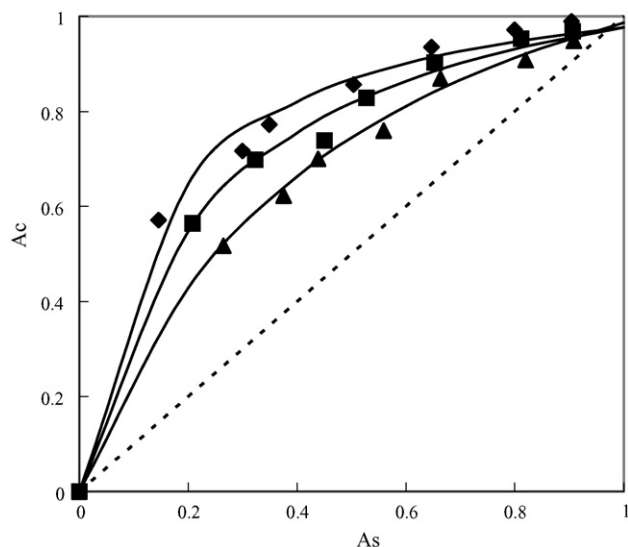


Fig. 2. Thermodynamic isotherms at different temperatures (20°C (◆); 40°C (■); 60°C (▲)).

Table 2

Langmuir parameters for sorption of ammonia by CaY at different temperatures

Temperature ($^\circ\text{C}$)	a	b	r^2
20	7.67	6.85	0.9787
40	4.99	4.11	0.9793
60	3.03	2.07	0.9799

3.3. Effect of temperature on the Kielland constant K_c

The Kielland constant K_c at different temperature can be calculated according to Eqs. (4) and (11). Fig. 3 describes the relation of K_c and T . It is clear that the value of K_c reduced with the temperature increasing. This is in agreement with the isotherms behavior discussed at Section 2.2. This phenomenon maybe caused by the following reason: the hydrated ionic radius of NH_4^+ and Ca^{2+} at higher temperature closed to the effective ionic radius aperture of clinoptilolite, and then the competition of NH_4^+ and Ca^{2+} come into being. So the selectivity of CaY for NH_4^+ reduced.

3.4. Kielland plots

The direct exchange Kielland plots were shown in Fig. 4. It showed that the value of K_c was not a constant, the relationship between $\ln K_c$ and A_c was approximate to linear. At the same time, the capacity of selectivity for NH_4^+ weakened with increased NH_4^+ concentration of solid (A_c), i.e. the adsorption ability reduced along with the advent of equilibrium.

3.5. Thermodynamic studies

As shown in Fig. 4, three isotherms had been obtained at 20 , 40 and 60°C . According to linear regression, the relation of $\ln K_c$ and A_c can be got, then the value of K_a can be calculated in terms of Eq. (5). The free energy (ΔG°) of the exchange reaction can be obtained from Eq. (6). The values

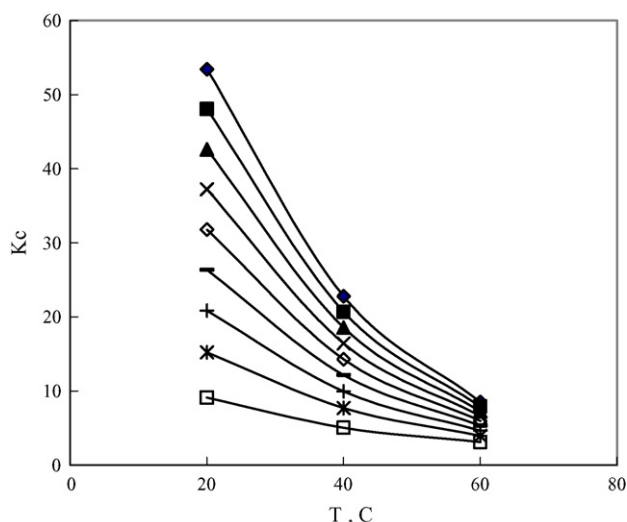


Fig. 3. Relation of K_c and T ($A_c = 0.1$ (◆); $A_c = 0.2$ (■); $A_c = 0.3$ (▲); $A_c = 0.4$ (×); $A_c = 0.5$ (◇); $A_c = 0.6$ (–); $A_c = 0.7$ (+); $A_c = 0.8$ (*); $A_c = 0.9$ (□)).

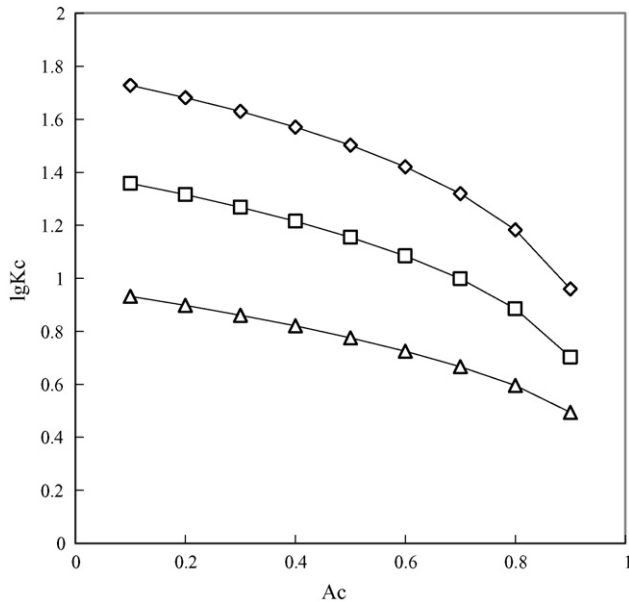


Fig. 4. Kielland plots for ion exchange (20 °C (◇); 40 °C (□); 60 °C (△)).

of ΔH° and ΔS° were determined from the slope and intercept of the plots of $\ln K_a$ versus $1/T$ according to Eqs. (7) and (8). All the values of thermodynamic parameters were shown in Table 3.

The results showed that the negative value of ΔG° confirmed that the feasibility of the process and spontaneous nature of exchange and adsorption with a high preference of ammonium on CaY, the negative value of ΔH° indicated that the exchange and adsorption process is exothermic-comporting with the previous discussion that the adsorptive ability to NH_4^+ decreased with increased temperature, and the negative value of ΔS° suggested that some structural changes of the CaY for ammonium. Simultaneously, negative value of ΔS° showed the decreasing randomness at the solid/liquid interface during the exchange of ammonium on the CaY.

3.6. Desorption and regeneration

A good adsorbent, in addition to its high adsorption capacity, must also exhibit a good regeneration ability for multiple uses. NH_4Y (clinoptilolite saturated by NH_4^+) can return to CaY in the $\text{Ca}(\text{OH})_2$ solution at 100–110 °C and NH_3 as by-product can be gained. The mass of clinoptilolite in this process and the adsorption capacity after regeneration were all shown in Table 4. It was clear that the mass of clinoptilolite was a constant in the 10 min and the adsorption capacity at pH 7 is also a constant after two times adsorption–desorption–readsorption cycles. The

Table 3
Thermodynamic parameters of clinoptilolite for NH_4^+

T (°C)	$\ln K_a$	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol K)
20	4.3244	−5.2698		−0.01673
40	3.5540	−4.6265	−0.3648	−0.01361
60	2.7313	−3.7826		−0.01026

Table 4
Data about desorption and regeneration of clinoptilolite

Regeneration time (min)	Mass (g)
0	10.1230
5	10.1201
10	10.1187
15	10.1185
S.E.	0.0021

Regeneration times	Adsorption capacity (mmol/l)
1	0.7928
2	0.7920
3	0.7906
4	0.7910
5	0.7909
S.E.	0.0010

results showed that the modified clinoptilolite can be regenerated once it approached its saturation capacity, allowing it to be used over a relatively long period of time. This result is a nice match for the literature [24,25]. So the CaY could be considered as a good exchanger for ammonium.

3.7. Simulated wastewater treatment

The treatment effect of CaY on simulated wastewater was shown in Fig. 5. As shown in figure, when the volume of outflow was 25 l, the effluent concentration of ammonium ion was 8.32, 7.01 and 5.52 mg/l for flowrates of 10, 40 and 70 ml/min, respectively. This concentration was far below 15 mg/l (Integrated wastewater discharge standard of China, GB8978-1996). Thereinto, the deviations in the values of Fig. 5 were about 0.236.

It can be observed that higher the flowrate is, lower the adsorption capacity is. As the flowrate of influent increases, the hydraulic retention time decreases, resulting in less ammonium ions being removed by clinoptilolite. Furthermore, the capacity

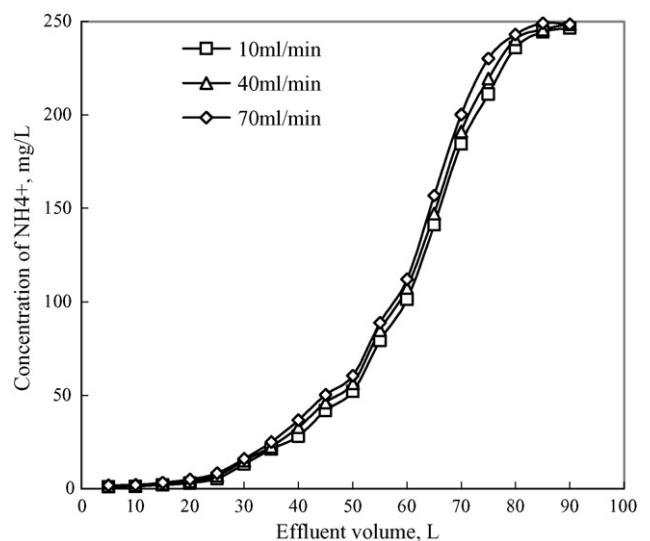


Fig. 5. Effect of flowrate on the ammonium removal by CaY (10 ml/min (□); 40 ml/min (△); 70 ml/min (◇)).

of clinoptilolite calculated by graphical integration of the area was 0.4597 mmol/g for 70 ml/min flowrate. The value is lower than the maximum capacity obtained previously. This might be due to the presence of other competitive cations in the simulated water, such as Na^+ , Ca^{2+} , K^+ and Mg^{2+} , which compete for the ion exchange sites of the clinoptilolite and inhibited the adsorption of ammonium ions. The specific results should be further confirmed.

Four loading and three regeneration cycles were carried out without finding the loss of ammonium removal capacity. These results indicate that $\text{Ca}(\text{OH})_2$ regeneration is effective.

4. Conclusions

The CaY has proved its superiority in ammonium removal on a laboratory scale. The following conclusions can be drawn from the results of the experiments in this study:

- The adsorption capacity for ammonium of CaY is impacted by pH values of ammonium solution, and the maximum adsorption capacity can be achieved at pH 6.
- CaY has a high selectivity to NH_4^+ . The temperature influenced the thermodynamic property of CaY. High temperature decreases the ammonium exchange.
- The data from experiments in batch study was applied to Langmuir isotherms and ammonium ion uptake onto CaY was accurately described by the Langmuir model.
- CaY can be cost effective regenerated with $\text{Ca}(\text{OH})_2$ and used time and again.
- CaY can be effective to use for removing the high concentration of ammonium nitrogen from simulate wastewater even though the presence of competitive ions (e.g. Na^+ , Ca^{2+} , K^+ and Mg^{2+}) partially reduced the removal capacity of ammonium.

As a summary, ammonium ion can be effectively and economically removed from wastewater using clinoptilolite modified by $\text{Ca}(\text{OH})_2$ solution.

Acknowledgement

The authors sincerely thank the financial support from the Key Technologies R&D Program of Hebei Province of China (No. 01276719D).

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