Ammonia removal from aqueous solution using natural Chinese clinoptilolite

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Abstract

This paper assesses the potential of natural Chinese clinoptilolite for ammonia removal from aqueous solution. In batch study, the effects of relevant parameters, such as contact time, pH and initial ammonia concentration were examined, respectively. The results show that although contact time needs at least 4 h in order to attain exchange equilibrium, ammonia removal by clinoptilolite occurs rapidly within the first 15 min of contact time; the pH has an effect on ammonia removal efficiency as it can influence both the character of the exchanging ions and the clinoptilolite itself; the ammonia removal capacity of clinoptilolite increases with the increase of initial ammonia concentration. In column study, clinoptilolite bed was exhausted at different flow velocities and ammonia breakthrough capacity of clinoptilolite bed was calculated. Furthermore, the optimum regeneration conditions were considered. The results show that flow velocity can affect breakthrough capacity of clinoptilolite by changing hydraulic retention time and the volume of 15–20 BV of 0.5 mol/L sodium chloride solution at pH 11–12 is sufficient for complete regeneration of clinoptilolite in column.
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1. Introduction

Ammonia nitrogen contributes to accelerated eutrophication of lakes and rivers, dissolved oxygen depletion and fish toxicity in receiving water. The most widely used traditional processes of ammonia removal are air stripping, ion exchange and biological nitrification–denitrification.

The efficiency of the process of air stripping and biological nitrification–denitrification is significantly impaired by the low temperature in winter. Ion exchange, therefore, is more competitive because of little influence of the low temperature in winter in the north of China, taking up relatively little space, and particularly its relative simplicity of application and operation.

Clinoptilolite, one of natural zeolites, has been found very effective in removing ammonia from water by means of its excellent ion exchange capacity since the seventies of last century. Many researchers have investigated ammonia removal from water by ion exchange [1–6]. Koon and Kaufman were concerned with ammonia removal from municipal wastewaters by clinoptilolite. Jørgensen et al. investigated the dependence of the efficiency and capacity of a European clinoptilolite on different parameters. Klieve and Semmens examined the effect of pretreatments on the performance of clinoptilolite for ammonia removal from wastewaters. Hlavay et al. investigated the optimal ion exchange conditions under which Hungary clinoptilolite could be used most effectively and economically for ammonia removal. Booker et al. studied the value of a natural Australian clinoptilolite as an efficient alternative to existing treatment processes of ammonia removal. Cincotti et al. examined Sardinian natural clinoptilolite to evaluate the adsorption for the metals and ammonium removal.

The main purpose of this study is to consider a kind of Chinese clinoptilolite, including defining various operational parameters necessary to remove ammonia efficiently from aqueous solution by ion exchange using this kind of Chinese

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clinoptilolite. Further study determines the most practical and effective regenerative conditions of this kind of clinoptilolite for reuse.

2. Experimental

2.1. Reagents

All chemicals used in the study were analytical grade reagents. All solutions and dilutions were made using distilled water. Ammonia nitrogen concentration in solution was analyzed by Nesslerization [7].

2.2. Characteristic of clinoptilolite

The clinoptilolite used as ion exchanger in the experiments was obtained from Jinyun, in the province of Zhejiang. The chemical composition of the clinoptilolite used in the study is shown in Table 1.

The chosen clinoptilolite was sieved into a grain size of 0.45–0.90 mm, then washed with distilled water to remove very fine particles and dried in an electric drying oven at 60 °C.

2.3. Batch study

2.3.1. Freundlich adsorption isotherm

Batch adsorption isotherm for the ammonia removal was investigated. Batch adsorption isotherm was determined in 500 mL conical flasks. Weighed amounts (1 g) of clinoptilolite were introduced into six conical flasks, to which 200 mL of ammonium chloride solution concentrations of between 2 and 94 mg NH_4^+-N/L at pH of about 6.0 were added.

The conical flasks were shaken for 4 h. Preliminary tests had confirmed that 4 h contact time was sufficient to make ammonium concentration in solution steady, which was assumed to reach equilibrium. At the designated time the two phases were separated by filtration through a 0.45 μm microporous membrane filter. The final ammonia concentrations remaining in solution were analyzed.

Table 1
Chemical composition of clinoptilolite

Component	%
SiO_2	65.52
Al_2O_3	9.89
Na_2O	2.31
K_2O	0.88
MgO	0.61
CaO	3.17
Fe_2O_3	1.04
MnO	0.06
TiO_2	0.21
H_2O	7.25
Loss of ignition	10.02

2.3.2. Total cation exchange capacity (CEC)

The ion exchange capacity of clinoptilolite may be given as the total CEC, which is defined by the number of equivalents of fixed charges per amount of zeolite. The total CEC indicates the theoretical amount of cations that can be accommodated by the clinoptilolite. However, the total CEC does not correspond to the operating exchange capacity, which is lower in practice.

The total CEC was measured by sodium and calcium cations displacement from the sodium-form clinoptilolite by potassium cations. To be converted to the sodium form, clinoptilolite was mixed in the solution of 0.1 mol/L sodium chloride and shaken at 90 °C for 24 h, then was thoroughly washed with distilled water and dried in oven at 60 °C prior to exchange capacity measurement. The total CEC measurement was accomplished by mixing 0.1 mol/L potassium chloride solution with a known weight of sodium-form clinoptilolites. Two phases were separated by filtration through a 0.45 μm microporous membrane filter after having been shaken for 24 h. Analysis of both sodium and calcium in solution yields the total cation exchange capacity of clinoptilolite.

2.3.3. Effect of contact time on clinoptilolite exchange performance

The rate of ammonia uptake by clinoptilolite from aqueous solution was investigated to determine the optimum time required for the ammonia–zeolite system to reach equilibrium. Ammonium chloride solution of different NH_4^+-N concentration of 200 mL was shaken and equilibrated with 1 g clinoptilolite, respectively. The equilibrium studies were performed for the time intervals ranging from 15 to 30 min and 1 h later. At the designated time the two phases were separated by filtration through a 0.45 μm microporous membrane filter. The initial and final ammonia concentrations remaining in solution were analyzed.

2.3.4. Effect of pH on clinoptilolite exchange performance

A 200 mL of ammonium chloride solution of 8.4 mg NH_4^+-N/L was prepared. The solutions were adjusted with hydrochloric acid or sodium hydroxide to pH values ranging from 4 to 10 and were equilibrated with 1 g of clinoptilolite. After having been shaken for 4 h, the two phases were separated by filtration through a 0.45 μm microporous membrane filter. The initial and final ammonia concentrations remaining in solution were analyzed.

2.3.5. Effect of ammonia concentration on clinoptilolite exchange performance

A 200 mL of ammonium chloride solution was equilibrated with 1 g clinoptilolite. The ammonia concentration range in the study was 2.1, 8.4, 18.3, 36.5, 56.4 and 94.2 mg NH_4^+-N/L at pH 6.0. The experiments of different initial NH_4^+-N concentration were performed, respectively. At the designated time the two phases were separated by filtration

through a 0.45 μm microporous membrane filter. The initial and final ammonia concentrations remaining in solution were analyzed.

2.4. Column study

In this investigation, column with an inner diameter of 20 mm was used. The bed height and volume of the clinoptilolite column were 20 cm and 60 cm^3, respectively. Column was filled with fine zeolite 0.45–0.90 mm.

In the column study, operation and regeneration parameters and ion exchange capacity of clinoptilolite were investigated. Peristaltic pump was employed to feed the stock solution to the clinoptilolite column. The ammonia nitrogen concentration of the samples collected from the column exit was monitored. The clinoptilolite column was exhausted by down flow at different flow velocities of 6, 12 and 24 BV/h, until an ammonia breakthrough of more than 5.0 mg NH$_4^+$–N/L was achieved. The column was then regenerated with sodium chloride solution at pH 11–12 and at different flow velocities of 5 and 10 BV/h. The regeneration solution was passed through the column in the down flow mode. The absence of ammonia in the effluent indicated the completion of regeneration. Another loading cycle was then carried out.

3. Results and discussion

3.1. Batch study

3.1.1. Freundlich adsorption isotherm

Freundlich isotherm is employed to describe the distribution of ammonium between the clinoptilolite phase and solution phase. The Freundlich model describes a logarithmic relationship between the solid and solution concentrations, and is useful in correlating isotherm data obtained over a wide range of concentrations [6,8–10].

The Freundlich equation is normally written as: $Q = KC^{1/n}$, where Q is the amount of ammonium adsorbed per unit weight of clinoptilolite; C the equilibrium concentration of ammonium remaining in solution; K and n are empirical constants ($n > 1$).

The Freundlich mode can be rearranged to the linear form by taking logarithms on both sides:

$$\log Q = \log K + \frac{1}{n} \log C$$

Plotting the experimental data using the above equation in Fig. 1 indicates that the model gives good fit for the data. The values of K and $1/n$ that best fitted the data as well as the corresponding correlation coefficient are presented in Table 2.

As a consequence, the Freundlich isotherm for ammonia removal on the raw clinoptilolite can be represented by the following empirical formula:
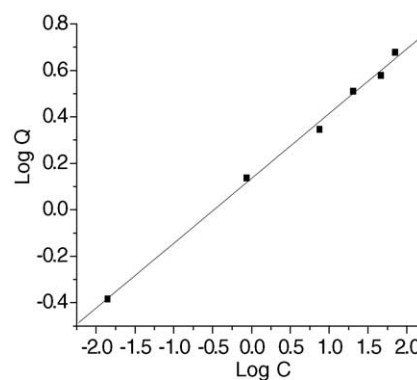
$$Q = 1.364C^{0.279}$$

Fig. 1. Linearised freundlich isotherm for ammonia removal by clinoptilolite.

3.1.2. Total cation exchange capacity

The results of the experiment show that the total CEC achieves 1.03 mmol/g, which is within the interval of 0.62 meq/g [2], 0.65 meq/g (9.15 mg NH$_4^+$–N/g) [4], 1.46 meq/g [11], 1.5 meq/g [5], 1.57–1.77 meq/g [3], 1.9 meq/g [1].

The study showed that clinoptilolite in raw form contained a complement of exchangeable potassium, sodium and calcium ions, but in exposing them to concentrated sodium chloride solution, each of the exchangeable ions could be displaced and clinoptilolite was then converted to single ionic form. The clinoptilolite in homoionic form, such as sodium-form, has much better cation exchange capacity [5,8,11,12]. The pretreatments that convert the clinoptilolite to sodium-form; however, may not be necessary because clinoptilolite is regenerated with sodium chloride solution in following column study and it turns more homoionic during regeneration process [13]. Jørgensen et al. concluded that regeneration solution of sodium chloride probably activated the materials [2].

3.1.3. Effect of contact time on clinoptilolite exchange performance

In experiments conducted in this study, it has been found that the ammonia removal by clinoptilolite occurred rapidly within the first 15 min of contact time; the removal rate of ammonia by clinoptilolite was initially fast, depending on the initial ammonia concentration; and then gradually decreased with increase in contact time. Booker et al. conducted batch experiments, which indicated that the adsorption of ammonia into the zeolite occurred rapidly within the first ten minutes of contact [5]. Dimova et al. also found that ammonia adsorption

Table 2
Freundlich model parameters for best fit and corresponding correlation coefficient

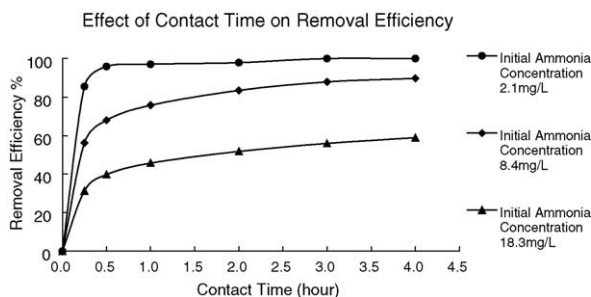| Parameter	Value
K	1.364
$1/n$	0.279
R^2	0.998

Fig. 2. Effect of contact time on clinoptilolite exchange performance.

to the zeolite was a fast process that occurred with less 15 min [14].

Fig. 2 shows that ammonia removal by clinoptilolite is high in the initial 15 min, but thereafter the rate significantly levels off and eventually approaches zero when equilibrium is attained. These changes in the rate of ammonia removal might be due to the fact that initially, all adsorbent sites were vacant and the solute concentration gradient was high. Afterwards the ammonia uptake rate by the clinoptilolite decreased significantly, due to decrease in adsorption sites. A decreasing removal rate, particularly at the end of the experiment, indicates a possible monolayer of ammonium ions on the outer surface and pores of the clinoptilolite and pore diffusion onto the inner surface of clinoptilolite particles through the film due to continuous shaking maintained during the experiment.

3.1.4. Effect of pH on clinoptilolite exchange performance

Fig. 3 shows the change of ammonia removal efficiency of clinoptilolite at pH values of 4–8 and 10 for given initial ammonium solution. The optimum removal efficiency is achieved when operating at pH value of 6. The result is consistent with the conclusion drawn by Koon and Kaufman [1].

pH has an obvious impact on ammonia removal by clinoptilolite since it 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.
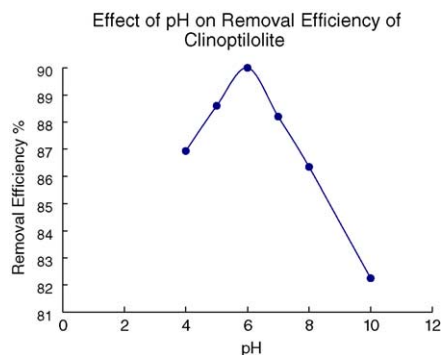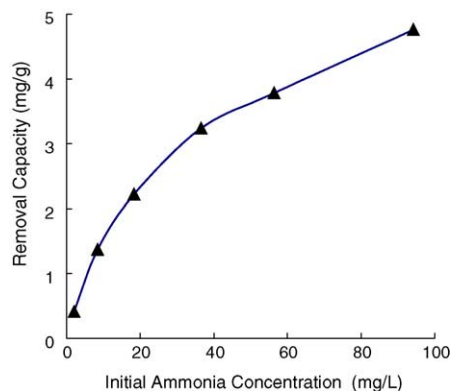

Fig. 4. Effect of initial ammonia concentration in aqueous solution on ammonia removal capacity of clinoptilolite.

ous ammonia. On the other hand, a variety of impurities that occupy micropores and macropores of clinoptilolite, such as calcium carbonate, unaltered glass, etc, are perhaps removed by hydrogen ions at lower pH [15]. This process contributes to improving the exchange capacity of clinoptilolite. It needs further study to prove.

3.1.5. Effect of ammonia concentration on clinoptilolite exchange performance

It can be shown in the experiments of this study that the ammonia removal capacity of clinoptilolite increases with the increase of initial ammonia concentration in solution (Fig. 4). Jørgensen et al. performed experiments and found that greater ammonia concentration resulted in a larger amount of adsorbed ammonia [12].

It can be interpreted by the fact that higher the ammonia concentration in solution is, higher the solute concentration gradient is; and it provides the necessary driving force so that ammonium ions could take the place of cations on the surface of the internal micropores of clinoptilolite within given contact time.

3.2. Column study

The concentration of ammonium chloride solution for column study was prepared at the level of 25.0 mg NH_4^+-N/L. It is shown in Fig. 5 that the breakthrough curves of ammonia removal by clinoptilolite at three different flow velocities.

The ammonia breakthrough capacity of clinoptilolite column was exhausted by loading 390, 355 and 305 BV influent when 5.0 mg NH_4^+-N/L effluent concentration was reached and the CEC of clinoptilolite calculated by graphical integration of the area above the breakthrough curves [1] was 7.74, 6.95 and 5.81 mg/g for flow velocity of 6, 12 and 24 BV/h, respectively. It can be observed that higher the flow velocity is, lower the breakthrough capacity is. As the flow velocity of influent increases, the hydraulic retention time decreases, resulting in less NH_4^+ being removed by clinoptilolite. Furthermore, we find that the capacity of clinoptilolite in column study is much higher than those in batch study, but lower than
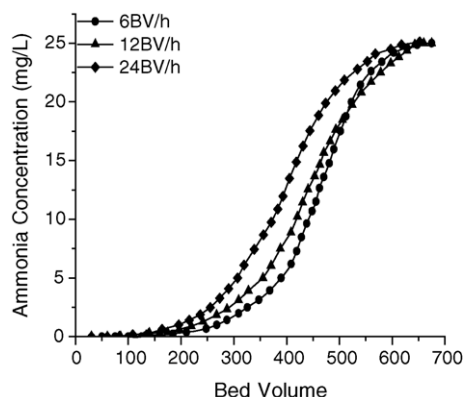

Fig. 3. Effect of pH on ammonia removal efficiency of clinoptilolite. The optimum removal efficiency is achieved when operating at pH value 6.

Fig. 5. Effect of flow velocity on the breakthrough curve of ammonia removal by clinoptilolite at 25 mg NH$_4^+$−N/L initial ammonium chloride solution.
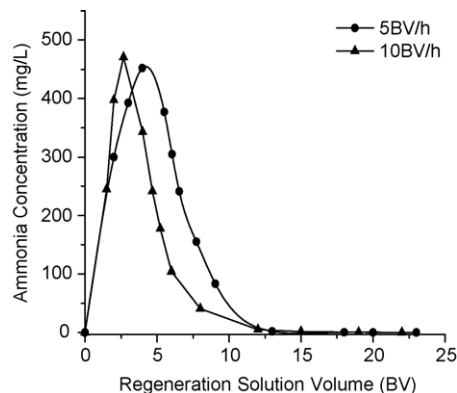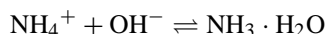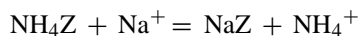

Fig. 6. Ammonia concentration in regeneration solution effluent at flow velocity of 5 and 10 BV/h. 15–20 BV of 0.5 mol/L sodium chloride regeneration solution at pH 11–12 is enough for nearly complete regeneration of clinoptilolite column.

total CEC and it achieves the exchange capacity of 53.7, 48.2 and 40.3% of total CEC for clinoptilolite in the experiments.

Six loading and five regeneration cycles were carried out without finding the loss of ammonia removal capacity. It is further observed that ammonia removal capacity of clinoptilolite was increased after the first regeneration. It shows that during the regeneration of the clinoptilolite column with sodium chloride solution, the clinoptilolite was changed into single ionic sodium-form, in which the clinoptilolite was found to improve its exchange capacity. After the following regenerations the loading process was repeated and it was found that the ammonia removal capacity of clinoptilolite remained constant. Jørgensen et al. also noted that the capacity of a sample of clinoptilolite increased with the number of regeneration. They concluded that the regeneration solution activated the clinoptilolite [2]. These results indicate that sodium chloride regeneration solution does not do any damage to ammonia removal capacity of clinoptilolite; instead, regeneration process can improve the ammonia removal capacity of clinoptilolite in column study.

3.3. Regeneration

Clinoptilolite columns were regenerated by 5 and 10 BV/h of regeneration solution—0.5 mol/L sodium chloride solution at pH 11–12 adjusted by using sodium hydroxide. Researchers found that the regeneration solution adjusted to pH > 11 can improve the regeneration efficiency and save the volume of regeneration solution required [1,4]. It was found that 15–20 BV of regeneration solution were sufficient to reduce ammonia concentration in regeneration solution effluent to lower than 0.5 mg NH$_4^+$−N/L (Fig. 6).

In addition, the pH value of regeneration solution effluent decreases rapidly during the initial stage of regeneration process and increases gradually to the pH of regeneration solution influent during the following process (Fig. 7). It is concluded that the depletion of hydroxide ions makes a great contribution towards ammonia removal from clinoptilolite. When the regeneration solution passed the column exhausted,

based on the following equations:

$$NH_4Z + Na^+ = NaZ + NH_4^+$$

$$NH_4^+ + OH^- \rightleftharpoons NH_3 \cdot H_2O$$

the ammonia concentration of regeneration effluent was very high so that there were no hydroxide ions in initial effluent and instead there was lots of NH$_4^+$. The hydrolyzation of lots of NH$_4^+$ in initial effluent led to the decreased pH of regeneration effluent. As the regeneration process was carried, the ammonia concentration of regeneration solution effluent decreased, finally tended to zero and at the same time the pH of the regeneration effluent gradually increased. When pH of regeneration effluent was within 11–12, the pH of regeneration solution influent, the regeneration process was completed.

No spent regeneration solution could be wasted since spent regeneration solution could be air-stripped to take out ammonia at pH 12–13 by the addition of more sodium hydroxide. In order to improve air-stripping efficiency, an amount of sodium carbonate was added into the spent regeneration solution. It can be shown in Fig. 8 that after 10 h of air-stripping, ammonia removal efficiency from spent regeneration solution can achieve 99%, and ammonia concentration in air-stripped
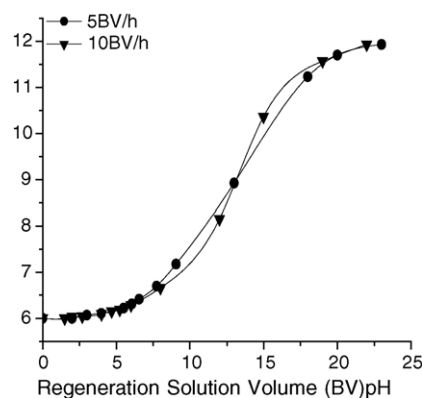

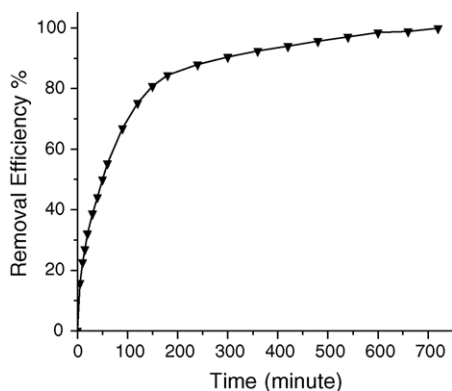Fig. 7. pH curve of regeneration solution effluent.

Fig. 8. Removal efficiency of ammonia in spent regeneration solution by air–stripping.

regeneration solution is lower than 0.5 mg NH_4^+−N/L. It can be reused for the next regeneration process cycle.

4. Conclusions

The Chinese clinoptilolite has proved its superiority in ammonia removal from synthetic solution on a laboratory scale. The following conclusions can be drawn from the results of the experiments in this study:

- The data from experiments in batch study were applied to Freundlich isotherm. Empirical formula obtained indicates that this kind of clinoptilolite has an excellent capacity of ammonia removal.
- The contact time has an effect upon ammonia removal efficiency. It spends at least 4 h for clinoptilolite attaining exchange equilibrium.
- pH value of synthetic ammonia solution influences ammonia removal efficiency. When pH value is about 6.0 at ammonia removal efficiency can achieve maximum.
- The different initial ammonia concentrations in solutions result in different CEC of clinoptilolite. The CEC of clinoptilolite increases with the increase of initial ammonia concentration ranging from 2 to 94 mg NH_4^+−N/L.
- Clinoptilolite in column study has much higher CEC than those in batch study, but much lower than total CEC, only achieves the half of total CEC. Flow velocity can affect breakthrough capacity of clinoptilolite by changing hydraulic retention time in clinoptilolite column. Clinoptilolite in column can achieve the highest ammonia removal capacity at the flow velocity of 6 BV/h since the hydraulic retention time is the longest.
- 15–20 BV of 0.5 mol/L sodium chloride regeneration solution at pH 11–12 are sufficient for complete regeneration of clinoptilolite in column without loss of ammonia removal capacity. On the other hand, the first regeneration process can improve the ammonia removal capacity of clinoptilolite because clinoptilolite can be converted to single ionic sodium-form during regeneration process. After the sec-

ond and third regeneration process, the ammonia removal capacity of clinoptilolite can remain constant.
- pH value of regeneration effluent decreases rapidly during the initial stage of regeneration process and increases gradually to the pH of regeneration influent during the following process. When the pH of regeneration effluent is within 11–12, the pH of regeneration influent, regeneration process is completed.
- Spent regeneration solution can be reused by air-stripping ammonia out of regeneration solution at pH 12–13.

Acknowledgement

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