

Ammonia removal from leachate solution using natural Chinese clinoptilolite

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Abstract

This paper assesses the potential of natural Chinese clinoptilolite for ammonia removal from the leachate solution of sewage sludge. In batch study the effects of relevant parameters, such as contact time, initial ammonia concentration and particle size of clinoptilolite, were examined respectively. The results show that the data obtained from batch studies were fit to Langmuir and Freundlich isotherms and the Langmuir isotherms reflect more reasonable for ammonium ion uptake onto clinoptilolite; the clinoptilolite adsorption process has been proved effective, at laboratory scale, the maximum adsorption capacity of the clinoptilolite, for ammonium concentration ranging from 11.12 to 115.16 mg NH₄-N L⁻¹ in leachate solution, was about 1.74 mg NH₄-N g⁻¹; the time to adsorption equilibrium was 2.5 h in leachate solution and 1.5 h more than for in NH₄Cl synthetic solution; ammonium adsorption increased with decreasing clinoptilolite particle size; the ammonia removal capacity of clinoptilolite increased with increasing initial ammonia concentration. It is believed that as adsorption agent for NH₄-N removal from sludge leachate, natural Chinese clinoptilolite can be feasible.

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1. Introduction

Today, our society generates substantial amounts of sewage sludge. As reported by Zorpas et al. [1], at Psittalia, approximately 750,000 m³ day⁻¹ of mainly municipal wastewater along with industrial wastes are subjected to primary treatment in China, producing approximately 250 tonnes day⁻¹ of dewatered anaerobically stabilized primary sewage sludge.

With the dramatic development of economy and improvement of human life, much more wastewater will be produced in China. On the other hand, people are concerned about environmental protection more than ever and relevant legislation or regulation is becoming more critical. The amount of wastewater treated and therefore the sewage sludge produced could increase rapidly in China [2]. Sewage sludge represents major byproducts of wastewater treatment. At a conventional sewage plant, sewage is first treated mechanically and then biologically. Then the sludge that was formed is further processed.

A variety of pollutants can be removed from the sewage by biological and chemical degradation, sorption to sludge or volatilisation [3]. So sewage sludge usually contains high proportions of organic matter and plant nutrients, but it also contains harmful elements, such as heavy metals, ammonium–nitrogen [4–6]. The major disposal options for sewage sludge include application to agricultural land, incineration, land reclamation, landfilling and so on. Considering both environmental and economical feasibility, sanitary landfilling is the most common disposal method for sewage sludge in China. Because of the initial moisture content of the sludge and other water inputs, such as raining, the leachates containing a range of soluble organic and inorganic contaminants are generated. One of the major environmental concerns associated with landfill of sewage sludge is related to the discharge of leachate into the environment, which may cause serious pollution and eutrophication of the groundwater aquifers as well as adjacent surface water.

The leachates generated from sewage sludge have high concentrations of organic compounds, a low pH value, high ammonia concentrations and high concentrations of heavy metals. Therefore, the leachate would lead to serious environmental problems if it was not properly treated. High ammonia con-

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centration can cause various serious problems, such as eutrophication. Ammonia nitrogen contributes to BOD in water due to its biologic oxidation by nitrifying bacteria, which can have a significant dissolved oxygen requirement for the breakdown of NH_3 into NO_3^- . In addition to the presence of nitrates, the principal end product of nitrification, stimulates algal growth and eutrophication in waterways. Therefore, a simple, efficient and economical treatment method for the leachate is needed.

Removal of ammonium can be accomplished through the use of air stripping, breakpoint chlorination, ion exchange, and biological nitrification–denitrification. The efficiency of the process of air stripping, biological nitrification and denitrification are significantly impaired by low temperature in winter. Ion exchange, therefore, is more competitive because of little influences of the low temperature during the winter in northern China, and particularly its relative simplicity and economy in 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 1970s of last century. Many researchers have investigated ammonia removal from water by ion exchange [7–11]. Koon and Kaufman [7] studied ammonia removal from municipal wastewaters by clinoptilolite. Jorgensen et al. [8] investigated the dependence of the efficiency and capacity of a European clinoptilolite on different parameters. Klieve and Semmens [9] examined the effect of pretreatments on the performance of clinoptilolite for ammonia removal from wastewaters. Booker et al. [11] studied the value of a natural Australian clinoptilolite as an efficient alternative to existing treatment processes of ammonia removal.

The purpose of this study is to consider a kind of Chinese clinoptilolite, to determine the adsorption capacity of the zeolite and examine the effects of particle size, ion concentration and contact time on the adsorption capacity of the zeolite to ammonium ions in the leachate solution.

2. Materials and methods

2.1. Clinoptilolite

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

Table 1
Chemical composition of clinoptilolite

Component	%
SiO_2	65.52 ± 1.46
Al_2O_3	9.89 ± 0.38
Na_2O	2.31 ± 0.10
K_2O	0.88 ± 0.06
MgO	0.61 ± 0.02
CaO	3.17 ± 0.23
Fe_2O_3	1.04 ± 0.06
MnO	0.06 ± 0.01
TiO_2	0.21 ± 0.03
H_2O	7.25 ± 0.83
Loss of ignition	10.02 ± 0.92

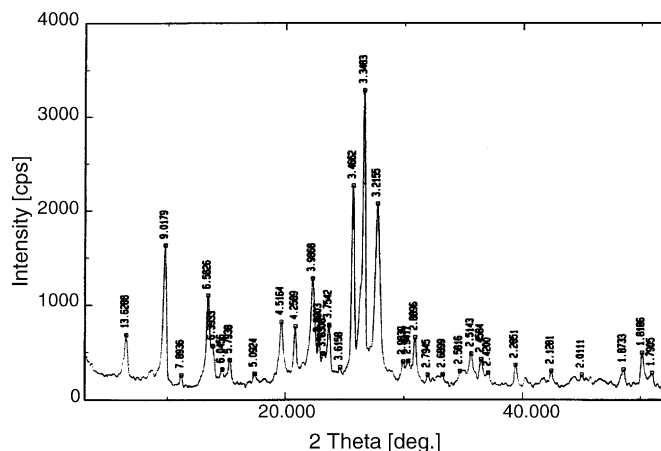


Fig. 1. The results of X-ray diffraction analysis.

The mineralogical features of clinoptilolite samples were determined using Rigaku D Max 2500 X-ray diffractometer using a step size of $5^\circ 2\theta \text{ min}^{-1}$ with $\text{Cu K}\alpha$ radiation generated at 40 kV and 150 mA. Analytical result showed that the main mineral in zeolite was clinoptilolite (Fig. 1).

The chosen clinoptilolite was sieved into three particle size: CLI1 (<20 mesh size, >0.90 mm), CLI2 (between 20 and 40 mesh, 0.45–0.90 mm), CLI3 (>40 mesh, <0.45 mm), then washed with distilled water to remove very fine particles and dried in an electric drying oven at 60°C .

2.2. Characteristics of the leachate

Leachate sample was collected from the main drain at the pilot scale sewage sludge landfill in Jizhuangzi wastewater treatment plant (WTP) in Tianjin, China. The leachate was delivered to laboratory and stored at 4°C before analysis. The characteristic of leachate is shown Table 2. All analysis methods were based on APHA [12] Standard methods for the examination of water and wastewater. The leachate was diluted into several levels of $\text{NH}_4^+\text{-N}$ concentrations with ammonia-free water.

Table 2
Characteristics of the leachate

Parameter	Concentration (mg L^{-1})
pH	7.53 ± 0.51
COD_{Cr}	110.5 ± 7.9
BOD_5	69.5 ± 4.8
TN	137.3 ± 4.25
$\text{NH}_4\text{-N}$	115.16 ± 3.84
TP	1.44 ± 0.056
PO_4^{3-}	0.062 ± 0.006
SS	120 ± 5.28
Na^+	69.1 ± 3.46
K^+	21.7 ± 1.01
Mg^{2+}	16.8 ± 0.85
Ca^{2+}	32.9 ± 1.73

2.3. Batch study

2.3.1. Kinetic experiments

Kinetic experiments were undertaken to study the effects of contact time on the ammonium adsorption capacity of the clinoptilolite. In this experiment, three particle size clinoptilolite were tested, the ammonium adsorption capacity of the clinoptilolite to leachate and NH_4Cl synthetic solution were examined, respectively. Weighed amounts (5.0 g) of clinoptilolite were put into each conical flask, to which 100.0 mL of solutions at pH of about 6.0 were added. Samples of 5.0 mL were extracted at certain time intervals from different conical flasks over the course of the experiment. 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.

2.3.2. Equilibrium experiments

Batch adsorption isotherm of ammonia removal was investigated. Batch adsorption isotherm was determined in 250 mL conical flasks. Weighed amounts (5.0 g) of clinoptilolite were introduced into each conical flask, to which 100.0 mL leachate solution whose concentrations were between 23.30 and 115.16 $\text{mg NH}_4^+-\text{N L}^{-1}$ at pH of about 6.0 were added. The conical flasks were shaken at 20 °C for 4 h. Preliminary tests had confirmed that 4 h contact time was sufficient to make ammonium concentration in the 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 the solution were analysed.

3. Results and discussion

3.1. Kinetic experiments

3.1.1. Effect of particle size on clinoptilolite exchange performance

Booker thought that two mechanisms generally control the rate of adsorption onto solid surfaces—either film diffusion or particle diffusion [11]. The adsorption rate varies inversely with square of particle radius for particle diffusion and particle radius for film diffusion. From Fig. 2, it is clear that the particle size of the clinoptilolite was an important factor in the ammonium adsorption capacity and adsorption rate. The results showed that the uptake of ammonium by clinoptilolite decreased with the increase of particle size. This was possibly due to greater available surface area on the smaller size particles of clinoptilolite. Results also showed that after equilibrium achieved there were no significant differences between different particle sizes. This was possibly due to the effect of zeolite particle size on the ammonium adsorption performance can be reduced by prolonged contact time (Fig. 2).

3.1.2. Effect of ammonia concentration on clinoptilolite exchange performance

The rate of ammonia uptake by clinoptilolite from the leachate solution was investigated to determine the optimum

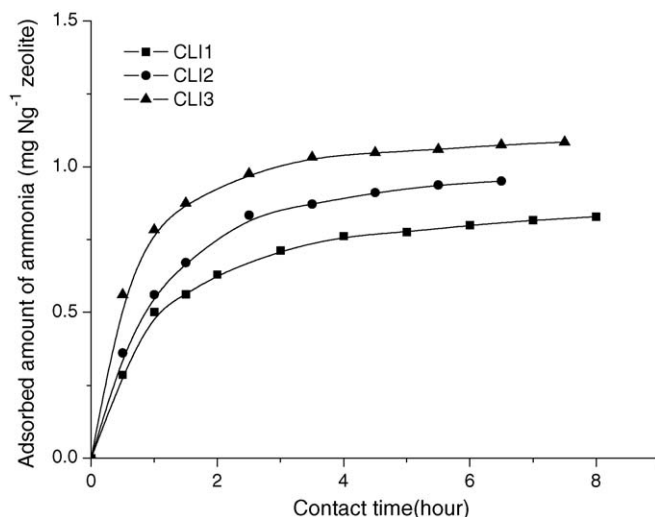


Fig. 2. Ammonia adsorption rate for different particle size of clinoptilolite NH_4^+-N 57.17 mg L^{-1} .

time required for the ammonia–zeolite system to reach equilibrium. The initial ammonium concentration in the leachate was determined and the amount of adsorbed ammonium ions in each set was calculated as a function of contact time. The particle size of CLI2 has wide representation in adsorption experiments. The CLI2 was chosen as an adsorbent in this study. All the data reported were the average values derived from duplicate samples.

The results of the analysis of the effects of ammonia concentration on the kinetics removal are shown in Fig. 3. The adsorption rate of ammonium by CLI2 was initially fast, at the first 1 h, depending on the initial ammonium concentration in the solution. Then the adsorption rate gradually decreased with increasing contact time. The data clearly showed the ammonia removal capacity of clinoptilolite increased with the increase of initial ammonia concentration in the solution and more than 80% of ammonia removal was achieved at the first 1 h when

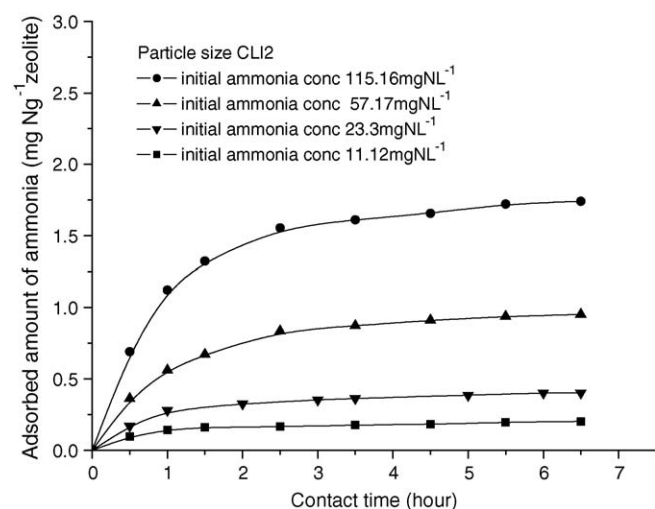


Fig. 3. Effect of initial ammonia concentration in the leachate on the exchange capacity.

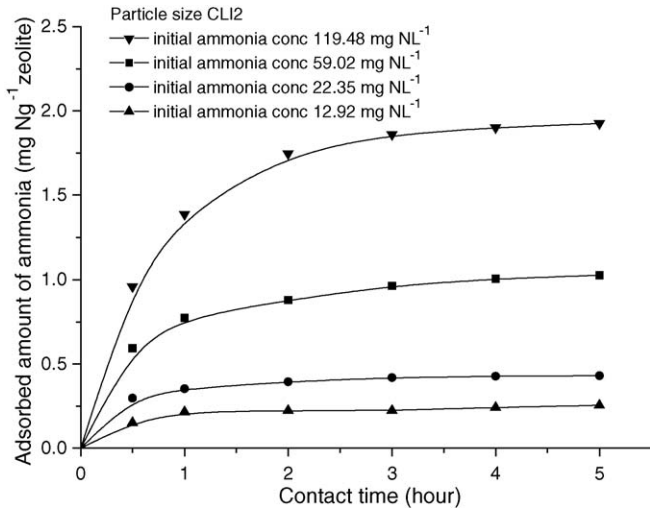


Fig. 4. Effect of initial ammonium concentration in the synthetic solution on the exchange capacity.

using CLI2. It can be interpreted by the fact that higher the initial ammonia concentration in the solution was, the higher the solute concentration gradient was, which provided the necessary driving force so that the ammonium ions could take the place of cations on the surface of the internal micropore of the clinoptilolite within the given contact time (Fig. 3).

The effects of initial ammonium concentration in the synthetic solution on the exchange capacity at the same condition with the leachate are shown in Fig. 4. Results of experiment showed that a higher ammonium ion adsorption to the NH_4Cl synthetic solution were observed than that to the leachate. In batch experiments, initial ammonia concentration of synthetic NH_4Cl solution were 12.92, 22.35, 59.02 and 119.48 mg L^{-1} , the ammonium adsorption amount of CLI2 were 0.254, 0.431, 1.027 and 1.926 $\text{mg NH}_4^+-\text{Ng}^{-1}$, respectively. When the concentration of the leachate were 11.12, 23.30, 57.17 and 115.16 mg L^{-1} , the ammonium adsorption amount of CLI2 were 0.202, 0.402, 0.951 and 1.74 $\text{mg NH}_4^+-\text{Ng}^{-1}$, respectively (Figs. 3–4).

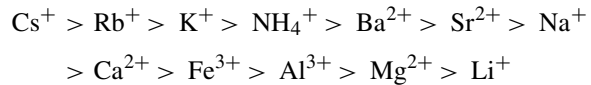
3.1.3. Effect of contact time on clinoptilolite exchange performance

In experiments conducted in this study, from Fig. 4, it is clear that the ammonium removal from NH_4Cl synthetic solution by CLI2 occurred rapidly within the first 30 min of contact time. The removal rate of ammonia by CLI2 was initially fast, depending on the initial ammonium concentration; then gradually decreased with the increase of contact time. Equilibrium

was achieved after 1 h. Booker et al. [11] conducted batch experiments, which indicated that the adsorption of ammonia upon the zeolite occurred rapidly within the first 10 min of contact time. From Fig. 3, however, the ammonium removal from the leachate by CLI2 occurred rapidly within the first 1 h of contact time and equilibrium was achieved after 2.5 h. It was possible that changes cation concentrations in the external solution affected the affinity for ammonium.

3.1.4. Effect of competitive cations on clinoptilolite exchange performance

Ames conducted experiments to rank cations according to their affinity to clinoptilolite and developed the following order [13]:



These series show that although some zeolites such as clinoptilolite have a high affinity and selectivity for ammonium ions, other ions in the solution have a negative impact on the ammonium exchange, especially the potassium which is adsorbed to the zeolites to at least the same extent as ammonium. Comparing the results obtained from NH_4Cl synthetic solution tests, the adsorption capacity to leachate solution reduced 10–20%. This might be due to the presence of other competitive cations in the leachate, such as K^+ , Na^+ , Mg^{2+} , and Ca^{2+} , which compete for the ion exchange sites of the clinoptilolite and inhibited the adsorption of ammonium. According to Koon and Kafmann [7], the ammonium exchange was investigated in relation to the total cation concentration of the influent. The exchange capacity decreased significantly up to a cation concentration of 0.01 M. This experiment results should be further confirmed.

3.2. Equilibrium experiments

3.2.1. Adsorption isotherm

As is known to all, ammonium ions are removed from aqueous solutions by zeolites via exchange with cations or by adsorption in pores of aluminosilicate systems. Ion exchange prevails when concentration of ammonium is equal or lower than the concentration of exchangeable cations of the zeolite, and adsorption begins to predominate with increased ammonium content [14]. Ammonium adsorption occurs by the ion exchange of ammonium ions with sodium, potassium, etc. at cation exchange sites of zeolites [15].

Freundlich isotherm is employed to describe the distribution of ammonium between the clinoptilolite phase and solution

Table 3
Fitted Freundlich and Langmuir parameters for sorption of ammonia by clinoptilolite

Material	Freundlich			Langmuir		
	K_f	$1/n$	r^2	a	b	r^2
CLI1	0.428 ± 0.021	0.458 ± 0.033	0.98 ± 0.01	2.128 ± 0.128	0.182 ± 0.011	0.99 ± 0.01
CLI2	0.596 ± 0.030	0.341 ± 0.025	0.93 ± 0.03	2.375 ± 0.184	0.186 ± 0.009	0.94 ± 0.02
CLI3	0.432 ± 0.023	0.496 ± 0.035	0.98 ± 0.01	2.469 ± 0.213	0.167 ± 0.014	0.98 ± 0.01

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 [16–18].

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 the solution, K and n are empirical constants ($n > 1$).

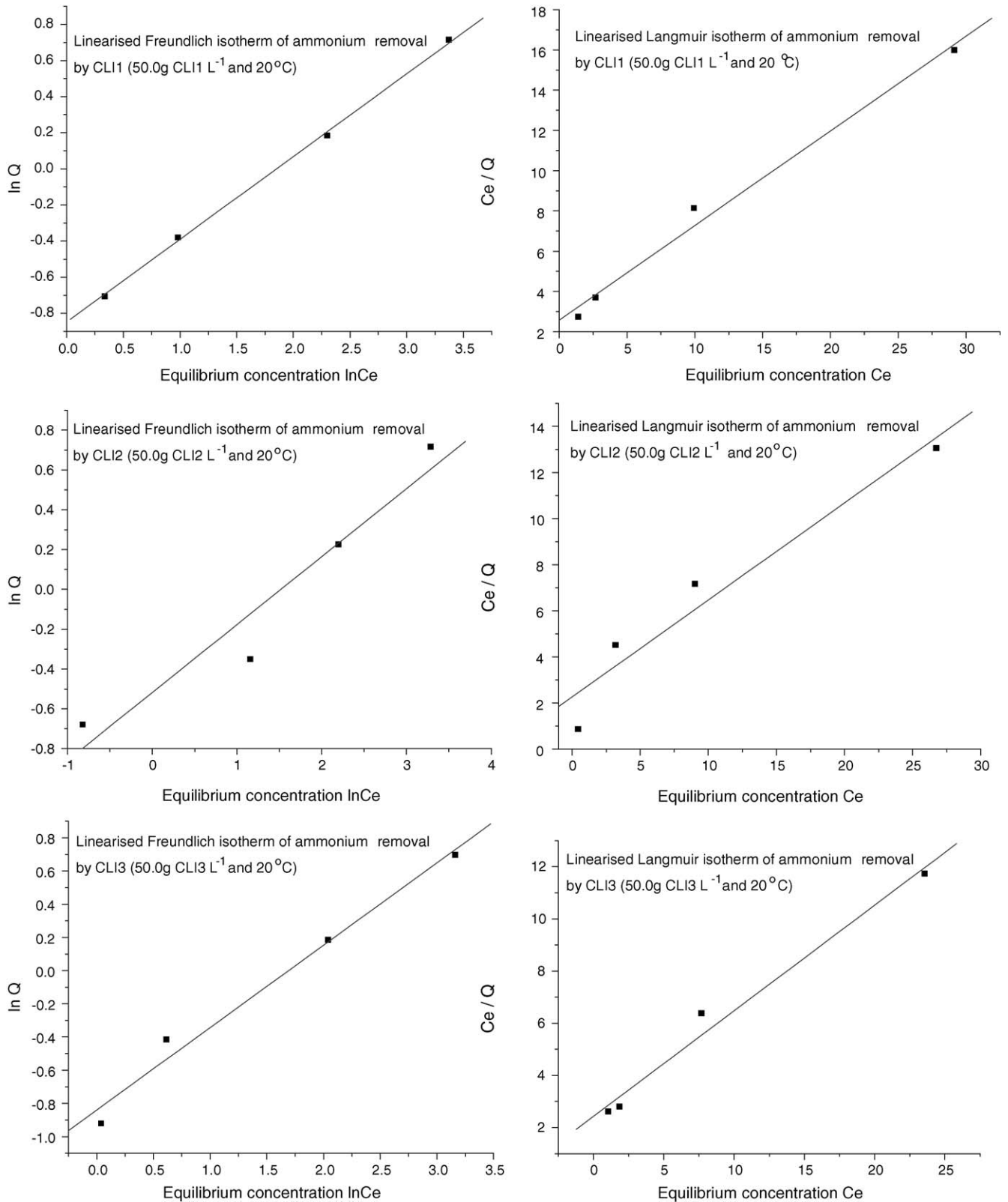


Fig. 5. Linearised Freundlich isotherm and Langmuir isotherm of ammonium removal by different particle size of clinoptilolite (50.0 g clinoptilolite L⁻¹ and 20 °C).

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

$$\text{Ln } Q = \text{Ln } K_f + \frac{1}{n} \text{Ln } C_e \quad (1)$$

The Langmuir equation is defined as $Q = abC_e / (1 + bC_e)$ where Q is the amount of ammonium adsorbed per unit weight of clinoptilolite, C_e the equilibrium concentration of ammonium remaining in solution, a and b are empirical constants. The constants in the Langmuir isotherm can be determined by plotting C_e/Q versus C_e and making use of the rewritten equation:

$$\frac{C_e}{Q} = \frac{1}{ab} + \frac{1}{aC_e} \quad (2)$$

Plotting the experimental data using Eqs. (1) and (2) in Fig. 5 indicates that both models give good fit for the data. The values of K_f , a , b , and $(1/n)$ that best fitted the data as well as the corresponding correlation coefficients are shown in Table 3.

Table 3 presents the results of the regression analysis for Freundlich and Langmuir isotherm model for different particle size of clinoptilolite considered in this research. It can be seen, that a very good fit to both model ($r^2 > 0.93$) was achieved. The data indicated that all batch experimental sorption data fit to the Freundlich and Langmuir adsorption models using least-squares regression. The Freundlich K values and Langmuir a values gave a measure of the relative ammonia adsorption capacity [18]. Comparing the results that we had obtained from previous experiment, Freundlich and Langmuir adsorption capacity, however, it seems that Langmuir isotherm truly reflects the adsorption capacity of the equilibrium tests and is more suitable for use in the analysis of adsorption capacity. The Langmuir isotherm also indicated that maximum ammonium adsorption (a values) increased with decreasing particle size of clinoptilolite.

4. Conclusions

The following conclusions can be drawn from the results of the experiments in this study:

1. The particle size distribution of the clinoptilolite has an impact on the ammonium adsorption capacity. The ammonia removal capacity of clinoptilolite increases with the decrease of particle size of clinoptilolite.
2. The ammonia removal capacity of clinoptilolite increases with the increase of initial ammonia concentrations in the leachate solution.
3. The presence of competitive ions (e.g. K^+ , Na^+ , Mg^{2+} , and Ca^{2+}) significantly reduced the removal capacity of ammonium. The ammonium adsorption capacity obtained by using the leachate was generally 10–20% lower than that using synthetic NH_4Cl solution.
4. The data from experiments in batch study was applied to Freundlich and Langmuir isotherms. The Freundlich and Langmuir isotherms gives an adequate correlation coefficient value and the Langmuir isotherm give a reasonable for ammonium ion uptake onto clinoptilolite. Empirical formula

obtained indicates that Chinese clinoptilolite has an excellent capacity of ammonia removal.

In the ammonia removal experiments, the result indicates that it is effective to use clinoptilolite for removing the high concentration of ammonium nitrogen from the leachate solution. The results may be also useful for the designing of landfill plants and the leachate treatment plants.

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