



Modification on natural clinoptilolite zeolite for its NH_4^+ retention capacity

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ABSTRACT

The scope of this study was to modify the natural clinoptilolite zeolite available locally (Akita Prefecture, Japan) for its ammonium ions retention capacity. The natural clinoptilolite was modified chemically and mechanically with changing time duration of sodium hydroxide treatment and ball to powder mass ratio in wet ball milling, respectively. The ammonium ions retention capacity of thus obtained modified clinoptilolites were found to sharply increase with either increasing alkaline metal cations content or increasing specific surface area (decreasing particle size) of the clinoptilolite. The main mechanism of ammonium ions retention is ion exchange and Na^+ ions were observed to be more easily exchanged for ammonium ions. The sorption isotherms were good fit to the Langmuir model in the cases of natural and chemically modified clinoptilolites while Freundlich model was favorable in the case of mechanically modified clinoptilolites. The maximum NH_4^+ retention capacities of natural clinoptilolite (NZeo), clinoptilolite treated with NaOH solution for 72 h (Zeo-72) and wet-milled clinoptilolite (WM-50) according to Langmuir model were 0.89, 1.15 and 1.39 mmol/g, respectively. The overall reaction is pseudo-second-order with rate constant of $3.6 \times 10^{-2} \text{ dm}^3 \text{ g}/(\text{mmol min})$. It was possible to enhance the NH_4^+ retention capacity of natural clinoptilolite just by decreasing particle size without incorporating any further exchangeable cations within the framework of zeolite.

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1. Introduction

Nitrogen compounds are essential for living organisms but 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. The traditional method for ammonium ion removal from municipal and industrial wastewaters is based on biological treatments [1]. However, as the discharge limits of different pollutants are more stringent, ion exchange and adsorption are gaining momentum as available methods for the treatment of waters polluted with ammonium ions.

Natural zeolites, which are aluminosilicate minerals and found in volcanogenic sedimentary rocks, possess several important properties including adsorption, cation-exchange, dehydration–rehydration, and catalysis. These natural zeolites have broad range of applications in construction materials, soil improvements for water and nutrient retention, treatment of water and wastewater for the removal of heavy metals and nutrients,

dietary supplements for farm-raised animals, health care, and other beneficial uses [2].

Clinoptilolite zeolites, $(\text{Na}_3\text{K}_3)(\text{Al}_6\text{Si}_{30}\text{O}_{72}) \cdot 24\text{H}_2\text{O}$, are one of the naturally existing zeolites. The theoretical cation-exchange capacity (CEC) of clinoptilolite is about 2.16 mequiv/g and is able to exchange ammonium-N with sodium and potassium [2]. This CEC has been utilized effectively for terrestrial agriculture, where clinoptilolites are first saturated with ammonium-N and then incorporated into crop soils. They act as a slow-release fertilizer, with plants able to extract the sequestered ammonia from the clinoptilolite [3–5]. Most of the manure ammonia sequestered in the zeolite is unavailable to nitrifying bacteria because of the small (4–5 Å) pore size of the crystal lattice structure [2]. Furthermore, clinoptilolites are also used for animal waste management, replacing clays in the cat litter market and are being used to create odorless, nitrogen-rich compost from farm livestock manures.

Although the ion exchange capacity of clinoptilolite is lower than some other zeolites, it generally exhibits a high selectivity for NH_4^+ ion. This zeolite has been broadly investigated as ion exchanger for ammonium ion removal due to its high selectivity [6–8]. The selectivity of ion exchange on this natural clinoptilolite was reported in an order of $\text{K}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$ [9–11]. The ammonium ion uptake capacity of sodium form of clinoptilolite was found enhanced with the presence of citric acid and whey protein during the uptake process [12]. A modification on clinoptilolite by incor-

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porating Ca ion was reported enhancing its ammonium ion uptake capacity [13].

Clinoptilolite is a silica-rich zeolite and has a lower ion exchange capacity in comparison to other zeolites. Furthermore, there are impurities like quartz in most of the clinoptilolite deposits. These factors reduce the uptake of ammonium ion onto natural clinoptilolite. The main aim of present work was to modify natural clinoptilolite mechanochemically for its higher ammonium ion retention capacity. The ammonium ion sorption isotherms of natural and modified clinoptilolite together with the rate of its retention by modified clinoptilolite were also investigated in this study.

2. Materials and methods

2.1. Sample preparation and characterization

The natural granules of clinoptilolite zeolite used in this study were obtained from the Futatsui area, Akita, Japan. This granular form of zeolites was ground manually to obtain in powder form by using mortar and pestle. The powder was then modified in two ways: in first case the powder was treated with *ca.* 4 M NaOH solution with sample solution ratio of 2 g:24 cm³ for 24, 48 and 72 h aging at room temperature. The solid sample was separated from solution by filtration and washed with distilled water for several times till the effluent became neutral to pH paper. Samples naming for thus obtained products were NZeo (natural zeolite), Zeo-24, Zeo-48 and Zeo-72 (zeolites treated with NaOH solution for 24, 48 and 72 h, respectively).

In second case, the powder sample was subjected to wet-milling in zirconia pot (0.08 dm³) with zirconia balls (2 mm Ø) in planetary ball mill (LA-PO.1, Ito Seisakusho Ltd., Japan) operating at 400 rpm for 24 h by using 0.03 dm³ distilled water and ball to powder mass ratios of 20, 30 and 50. After wet-milling, the slurry was filtered, washed and dried at 80 °C for overnight. The solid samples were designated as WM-20, WM-30 and WM-50 (WM for wet-milled followed by ball to powder mass ratio).

Powder X-ray diffraction (XRD) patterns were obtained using an X-ray diffractometer with monochromated Cu K α radiation (JDX-3530, JEOL, Japan). The chemical compositions of the samples were analyzed by X-ray fluorescence (RIX2000, Rigaku, Japan). The specific surface area and texture of wet-milled samples were obtained by the BET method using a BELSORB-Mini instrument (BEL, Japan) and Scanning Electron Microscope (JSM-5900LV, JEOL, Japan), respectively.

2.2. NH₄⁺ uptake experiment

The uptake of NH₄⁺ was performed with aqueous NH₄Cl solution (Wako, Japan) on NZeo, Zeo-24, Zeo-48, Zeo-72, WM-20, WM-30 and WM-50 under the following conditions: reaction temperature, 25 °C; sample/solution ratio, 0.1 g/0.05 dm³; initial NH₄⁺ concentration, 28.22 mmol/dm³; reaction time, 24 h. The solution pH was measured just at the time of putting the sample into the solution (initial pH) and after the reaction (equilibrium pH). In the second step, NH₄⁺ uptake experiments were performed on NZeo, Zeo-72 and WM-50 as a function of the initial NH₄⁺ concentration (range: 1.47–28.2 mmol/dm³), with other parameters as above. The kinetic study of the uptake of NH₄⁺ was carried out with Zeo-72 sample with reaction time variation (range: 10, 30, 60, 180, 360, 720 and 1440 min) under the following conditions: reaction temperature, 25 °C; sample/solution ratio, 0.1 g/0.05 dm³; initial NH₄⁺ concentration, 28.22 mmol/dm³.

After the uptake experiments, the samples were filtered and washed frequently with distilled water. The original NH₄⁺ solution (prior to uptake) and separated solutions (after uptake) were chem-

Table 1

The chemical compositions of natural and NaOH treated clinoptilolites.

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	CaO	MgO	K ₂ O
NZeo	77.96	14.02	1.30	1.15	1.23	0.46	3.88
Zeo-24	74.80	14.10	1.26	4.44	1.60	0.91	2.89
Zeo-48	74.60	14.30	1.61	3.62	1.75	1.15	2.97
Zeo-72	73.74	14.78	1.62	4.03	1.74	1.15	2.94

ically analyzed for NH₄⁺, Na⁺, K⁺ and Ca²⁺ by ion chromatograph (DX-120, DIONEX, USA) for three times and the average data were used for experimental analysis. The uptake % and uptake (mmol/g) were calculated using the following formulae:

$$\text{uptake (\%)} = \frac{C_i - C_{eq}}{C_i} \times 100$$

$$\text{uptake (mmol/g)} = \frac{(C_i - C_{eq})V}{M}$$

where C_i , C_{eq} , V and M are the initial concentration (mmol/dm³), equilibrium concentration (mmol/dm³), volume of solution (dm³) and mass of sample (g), respectively.

3. Results and discussion

3.1. Sample characterization

The chemical compositions of natural and NaOH treated clinoptilolites are shown in Table 1. The XRD patterns of as-received-ground (NZeo) and NaOH treated clinoptilolite samples (Zeo-24, Zeo-48 and Zeo-72) are shown in Fig. 1. There was no appreciable change in the XRD patterns of natural clinoptilolite after NaOH treatment with time variation which indicates no structural change with the incorporation of exchangeable sodium ions to the natural zeolite.

Ball-milling is one of the most widely used techniques to reduce the particle size of ceramic materials. This technique consists of placing the particles to be ground in a container with grinding media (here in the present case ZrO₂ balls). The particles move

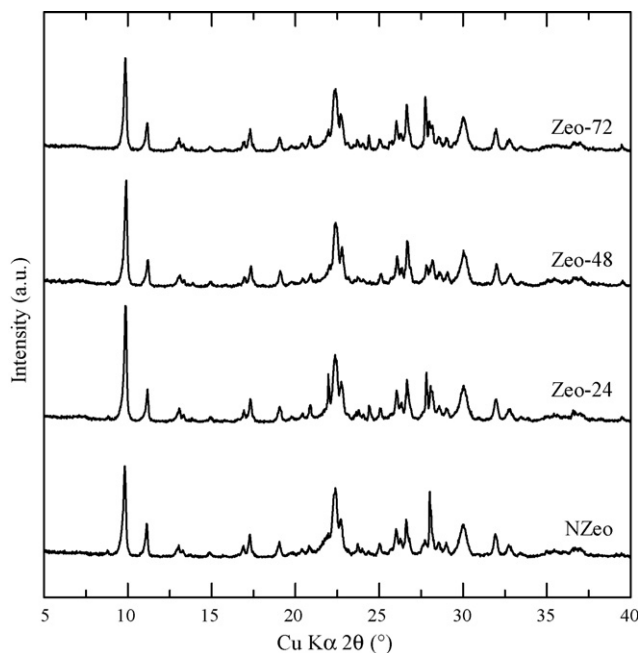


Fig. 1. XRD patterns of as-received and ground (NZeo) and NaOH treated clinoptilolite samples with time variation.

between the much larger balls and in between balls and wall of the container and effectively broken into the successive smaller particles. The XRD patterns of the original and ball-milled samples with the variation of ball to powder mass ratio are shown in Fig. 2. With the increase of ball to powder ratio or by reducing the amount of powder at fixed amount of balls, the amorphous nature of the sample was found enhanced. Almost complete amorphous form of clinoptilolite was obtained with ball to powder mass ratio of 50. This effect is attributed to the fact that the greater ball to powder ratio increases the collision frequency which in turn leads to faster diffusion process [14]. The SEM micrographs of all the three types of wet-milled samples (WM-20, WM-30 and WM-50) together with the manual ground clinoptilolite (NZeo) are shown in Fig. 3 which gives an approximate idea of particle size distribution variation.

3.2. Factors responsible for NH_4^+ retention capacity

The sorption is either external or internal diffusion controlled mechanism. The external diffusion is the transfer of the sorbed species from the bulk of fluid to the surface of the particle while the internal diffusion occurred in the macro/meso and micro sized pores involves the transfer of the species to the active sites of the sorbent [15]. Hence, there are two major factors which have positive influence over the NH_4^+ retention capacity of clinoptilolite, i.e. either by increasing relative content of alkaline metal cations (exchangeable cations) or by decreasing zeolite particle size

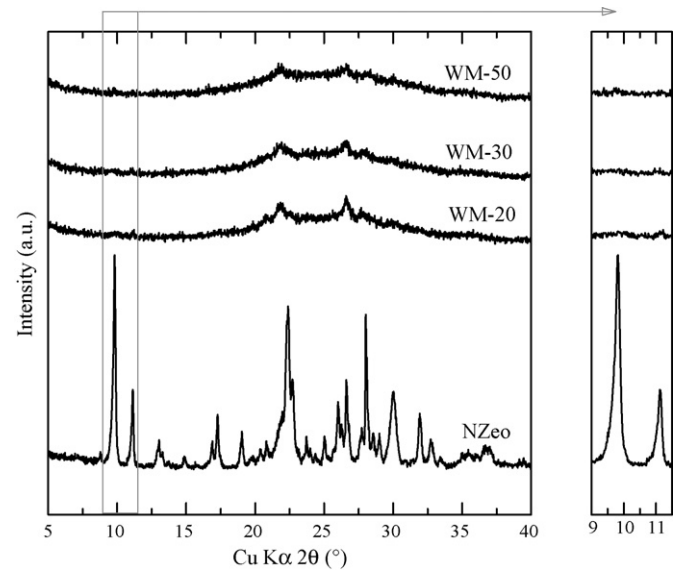


Fig. 2. XRD patterns of as-received and ground (NZeo) and wet-milled clinoptilolite samples with ball to powder mass ratio variation.

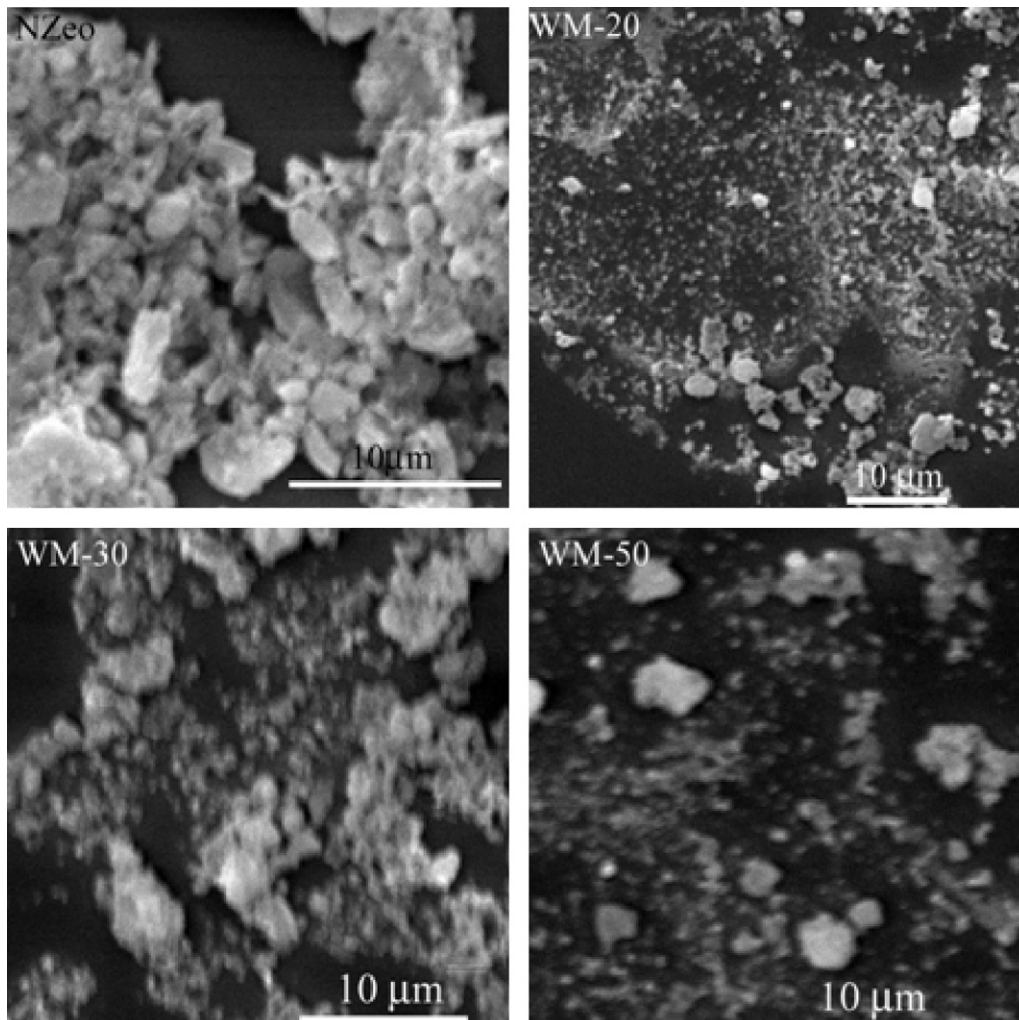


Fig. 3. SEM micrographs of manual ground and wet-milled clinoptilolite samples.

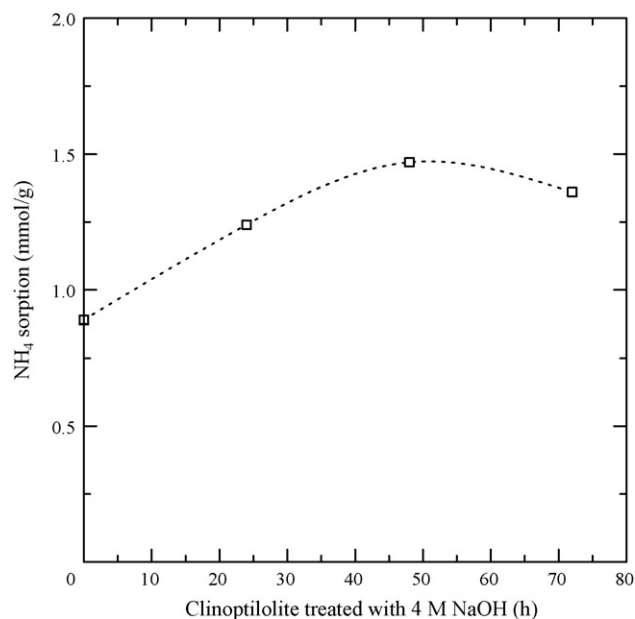


Fig. 4. NH_4^+ sorption as function of treatment time of clinoptilolite with 4 M NaOH aqueous solution.

(increasing surface area) [16] which is in accordance with previous report [17] and also with the adsorption of Zn^{2+} on Bigadic zeolite [18].

The NH_4^+ uptake properties of four samples, namely, NZeo, Zeo-24, Zeo-48 and Zeo-72 were determined at fixed initial NH_4^+ concentration (28.22 mmol/dm^3) in order to evaluate the impact of the incorporation of exchangeable Na^+ to the natural clinoptilolite (as there was no release of Ca^{2+} during the uptake of NH_4^+ , we have not considered Ca^{2+}). The NH_4^+ sorption of alkali treated clinoptilolites were found sharply increased to that of natural clinoptilolite and the average trend of NH_4^+ sorption as a function of alkali treatment time of clinoptilolite is in increasing order as shown in Fig. 4. The NH_4^+ sorption is in general enhanced with the increase of exchangeable ions on sorbent. This may be either the high Na^+ concentration during treatment essentially places exchangeable ions onto sites which are in relatively homogenous areas of the clinoptilolite or enhances access to relatively inaccessible sites. The obtained data for NH_4^+ sorption as a function of released Na^+ and K^+ are shown in Fig. 5. Though the experimental data are much more scattered, majority of data are in the vicinity of the ideal line for complete ion exchange mechanism. Furthermore, the release of Na^+ was found much higher in comparison to the release of K^+ . These facts indicate that the main mechanism of NH_4^+ sorption of present samples is ion exchange with mainly Na^+ together with external diffusion.

The wet-milled samples were just dried separately by heating so expected to have no change in their chemical composition from that of the natural clinoptilolite (NZeo) after mechanical treatment except that of particle size or nature of the powder. The particle size of clinoptilolite (NZeo) was about $2.5 \mu\text{m}$ while after milling it reduced to $<1 \mu\text{m}$ and the NH_4^+ sorption capacity was 1.39 mmol/g . In previous reports, the NH_4^+ sorption capacities of Turkish clinoptilolite of the size range of $1.0\text{--}1.4 \text{ mm}$, Na-clinoptilolite of the size range of $0.5\text{--}0.71 \text{ mm}$ from New Zealand and Na-clinoptilolite of the size range of $0.25\text{--}2.36 \text{ mm}$ from USA were 0.45 , 0.66 and 1.14 mmol/g , respectively [19,20,6].

The wet-milling enhances the reduction of particle size and thereby increased the specific surface area of samples. The NH_4^+ sorption capacity of these three samples together with NZeo as a function of the specific surface area is shown in Fig. 6. The sharp

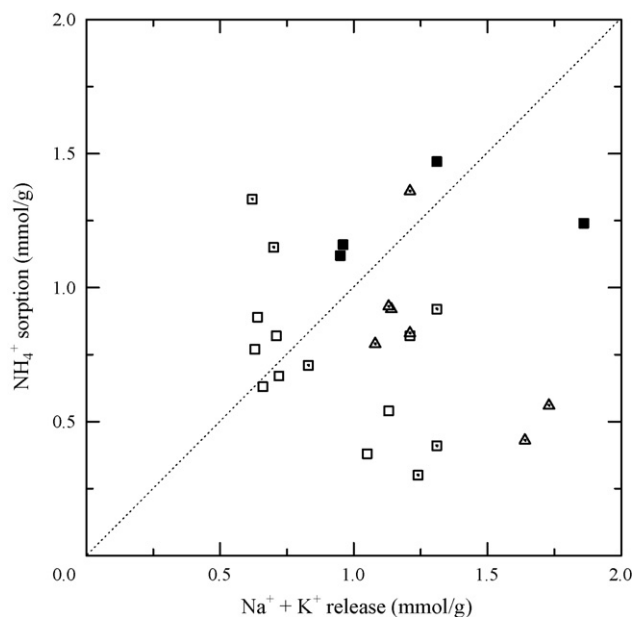


Fig. 5. NH_4^+ sorption of present sorbents as a function of released Na^+ + K^+ into the solution. The symbols are as follows: (□) NZeo; (◑) WM-50; (▲) Zeo-72; (■) WM-20, WM-30, Zeo-24 and Zeo-48.

increase of NH_4^+ sorption with the increase of specific surface area of the sorbent due to the reduction of particle size indicates the dominance of external controlled diffusion mechanism rather than ion exchange.

3.3. NH_4^+ sorption isotherms

The sorption isotherms of NH_4^+ were simulated by the mathematical equations of Langmuir [21] and Freundlich [22]. The Langmuir model assumes that the removal of ammonium ion occurs on a homogenous surface by monolayer sorption, and predicts a linear relation between (C_e/Q_e) and C_e :

$$\left(\frac{C_e}{Q_e}\right) = \left(\frac{1}{Q_{\max}}\right) C_e + \left(\frac{1}{Q_{\max}b}\right) \quad (1)$$

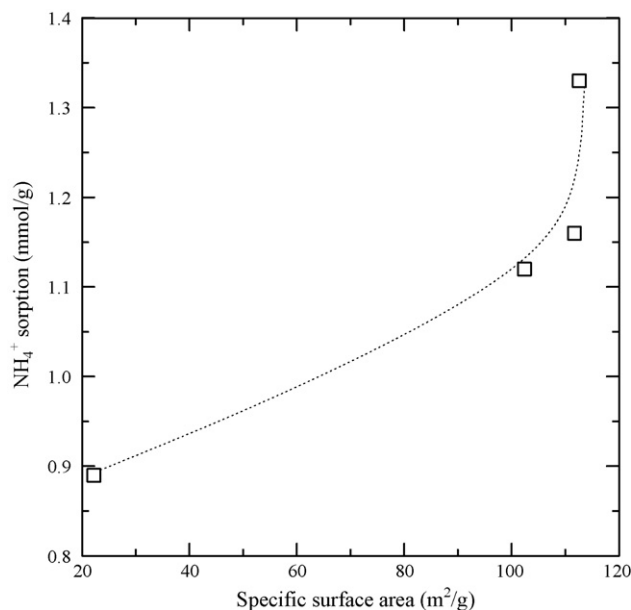


Fig. 6. NH_4^+ sorption as a function of specific surface area (BET) of sorbent materials.

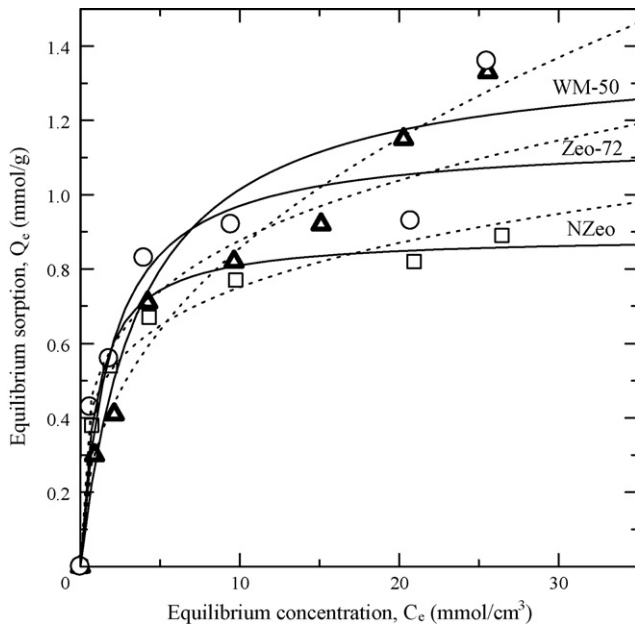


Fig. 7. NH_4^+ sorption isotherms of natural and modified clinoptilolites. Solid and broken lines represent predicted data obtained from Langmuir and Freundlich parameters. The symbols are as follows: (\square) NZeo; (Δ) WM-50; (\circ) Zeo-72.

where C_e (mmol/dm^3) is the equilibrium concentration, Q_e (mmol/g) is the amount sorbed at equilibrium, Q_{max} (mmol/g) is the monolayer sorption capacity and b (dm^3/mmol) is the Langmuir constant.

On the other hand, the Freundlich model, which assumes the surface heterogeneity and exponential distribution of active sites, provides an empirical relationship between the sorption capacity and equilibrium constant of the sorbent. The mathematical representation of this model is:

$$\log Q_e = \frac{1}{n} \log C_e + \log K_f \quad (2)$$

where K_f [$(\text{mmol}/\text{g})(\text{dm}^3/\text{mmol})^{1/n}$] and n (g/dm^3) are the Freundlich constants related to the sorption capacity and sorption affinity of the sorbent, respectively. Q_e and C_e are similar as Eq. (1).

NH_4^+ uptake experiments with the variation of initial NH_4^+ concentration ranging 1.47–28.22 mmol/dm^3 were performed on three samples namely NZeo, Zeo-72 and WM-50. The natural clinoptilolite (NZeo) was selected to obtain its NH_4^+ sorption capacity without any modification while Zeo-72 and WM-50 samples were selected to study the impact of its NH_4^+ sorption capacity by modifying its chemical composition and specific surface area (by changing from crystalline to amorphous form), respectively. The resulting sorption isotherms are shown in Fig. 7. The parameters calculated from the Langmuir and Freundlich equations using the experimental data are listed in Table 2. The solid and broken lines in Fig. 7 are calculated from the resulting Langmuir and Freundlich parameters. The correlation coefficient values indicate the sorption

Table 2
Langmuir and Freundlich parameters for NH_4^+ sorption by natural and modified clinoptilolites.

Sorbent	Langmuir model				Freundlich model		
	Q_{max}	b	R^2	ΔG	K_f	n	R^2
NZeo	0.89	1.01	0.9956	−17	0.46	4.67	0.9391
Zeo-72	1.15	0.54	0.9025	−16	0.50	4.10	0.8376
WM-50	1.39	0.27	0.9350	−14	0.32	2.34	0.9691

Table 3

The NH_4^+ sorption capacity (in mmol/g) of several other natural and modified clinoptilolite zeolites.

Sorbent	Q_{max}	Reference
New Zealand's clinoptilolite	0.32	[24]
Turkish natural clinoptilolite	0.45	[19]
China's natural clinoptilolite	0.58	[10]
New Zealand's clinoptilolite (Na-form)	0.66	[20]
China's natural clinoptilolite (Ca-form at pH 6)	0.82	[13]
Akita's natural clinoptilolite	0.89	Present work
China's natural clinoptilolite-chemically modified	1.07	[10]
USA's clinoptilolite (Na-form at pH 6)	1.14	[6]
USA's clinoptilolite (Na-form at pH 9)	1.15	[6]
Akita's natural clinoptilolite-chemically modified	1.15	Present work
Akita's natural clinoptilolite-mechanically modified	1.39	Present work
Commercial clinoptilolite from Hector deposit	1.61	[20]
Scotland's clinoptilolite (Na-form)	1.61	[12]
Commercial clinoptilolite	1.76	[20]

isotherms were good fit to the Langmuir model in cases of natural and chemically modified clinoptilolites while Freundlich model was favorable in case of mechanically modified clinoptilolite. These behaviors are expected to be due to not change in the crystalline structure of clinoptilolite during chemical modification while during mechanical modification the crystalline structure was crushed and hence heterogeneity factor came into existence.

According to the Langmuir data, the maximum NH_4^+ sorption capacity (Q_{max}) of natural zeolite (NZeo) is about 0.89 mmol/g while that of WM-50 is 1.39 mmol/g and the resulting Q_{max} values increase in the order WM-50 > Zeo-72 > NZeo. The NH_4^+ sorption capacity of previously reported some of the other natural and modified clinoptilolites together with present samples are shown in Table 3. The NH_4^+ sorption capacity of present natural clinoptilolite is relatively higher than previously reported for natural clinoptilolites. The variation in the NH_4^+ sorption capacity of clinoptilolite from various resources is due to the difference in the relative content of alkaline metal cations and chemical-physical pre-treatment techniques. The commercial clinoptilolites have much higher NH_4^+ sorption capacity in comparison to present modified clinoptilolites. The possible reason for such a higher sorption capacity may be the clinoptilolite for the commercial market would probably be pre-screened and pre-treated to yield an optimal performance by removing inert components [20].

The Langmuir constant b is related to the free energy change of sorption (ΔG , kJ/mol) according to the following formula [23]:

$$\Delta G = -RT \ln(1000b) \quad (3)$$

where R is the gas constant (8.314 $\text{J}/(\text{mol}\cdot\text{K})$) and T is the temperature (K). The Gibbs free energy indicates the degree of spontaneity of the NH_4^+ sorption process, negative values reflecting a more energetically favorable sorption process. The ΔG values obtained from Eq. (3) are listed in Table 2, confirming the feasibility of all the sorbents and the spontaneity of the sorption process.

3.4. NH_4^+ sorption kinetics

Fig. 8 shows NH_4^+ sorption and t/Q_t of Zeo-72 as a function of contact time. The NH_4^+ sorption-time plot indicates that the sorption progresses in two steps. The first step is the rapid sorption of the NH_4^+ within 60 min, with a slower second step during which equilibrium is attained. This rapid sorption of NH_4^+ by chemically modified clinoptilolite for about 60 min and thereby attaining towards equilibrium is in accordance with the previous report [25]. The rapid step is thought to be due to the abundant availability of active sites on the sorbent material, and as these sites become increasingly occupied, the sorption becomes less efficient and slower.

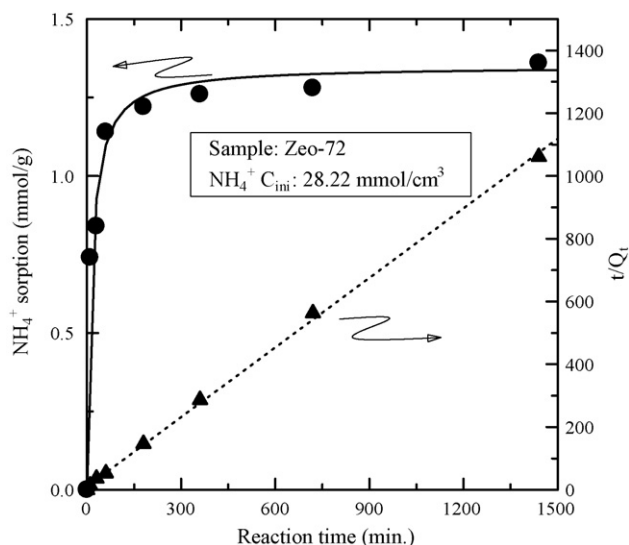


Fig. 8. NH_4^+ sorption and t/Q_t of Zeo-72 as a function of contact time. Solid and broken lines represent predicted data obtained from Ho et al.'s pseudo-second-order equation parameters.

Table 4
Kinetic data of NH_4^+ sorption for Zeo-72 obtained from two equations.

K_1 from Eq. (4)	K_2 from Eq. (5)	Q_e (mmol/g) from Eq. (4)	Q_e (mmol/g) from Eq. (5)
3.5×10^{-3}	3.6×10^{-2}	0.694	1.36

In order to investigate the rate law describing the NH_4^+ sorption, the kinetic data obtained from the batch experiments were analyzed using three kinetic equations, namely, the first-order equations proposed by Lagergren and Svenska [26] and the pseudo-second-order equation proposed by Ho et al. [27]. The equations were rearranged to obtain the linear forms, as follows:

$$\log_{10} (Q_e - Q_t) = \log_{10} Q_e - \frac{K_1}{2.303} t \quad (4)$$

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{1}{Q_e} t \quad (5)$$

where Q_t is the amount sorbed (mmol/g) at time t (min), Q_e is as in Eq. (1), and K_1 and K_2 are rate constants of Eqs. (4) and (5), respectively. Eqs. (4) and (5) yielded the rate constants (K_1 and K_2) and the equilibrium NH_4^+ sorption Q_e , presented in Table 4. The Q_e value obtained from the pseudo-second-order Eq. (5) is comparable with the Q_{max} value obtained from the Langmuir Eq. (1) (Table 2) together with the straight line plot of t/Q_t versus t of Fig. 8, indicating the pseudo-second-order reaction model is the most appropriate for NH_4^+ sorption by the present sorbent. The kinetic data obtained from the NH_4^+ uptake of present work will be helpful for mass transfer parameters in fixed-bed ion exchange columns, operating under non-equilibrium conditions.

4. Conclusion

The overall ammonium ion retention behavior of the clinoptilolite produced in Akita Prefecture, Japan is similar to that of clinoptilolite obtained from other resources. The present clinoptilolite has a high affinity for ammonium ion, which is observed across a range of ammonium ion concentrations of interest in the context of water treatment. The NH_4^+ retention capacity of natural clinoptilolite is enhanced either by increasing alkaline metal cations content with chemical modification or by reducing particle size or increasing specific surface with mechanical modification.

It was possible to enhance the NH_4^+ retention capacity of natural clinoptilolite just by decreasing particle size without incorporating any further exchangeable cations within the framework of zeolite in present study. The results show that the combined effect, i.e. mechanochemical modification on natural clinoptilolite which can increase both alkaline metal cations content and surface area will further enhance the overall NH_4^+ retention capacity of natural clinoptilolite. Furthermore, the kinetic data of the NH_4^+ retention on clinoptilolite will be helpful to construct mass transfer parameters in fixed-bed ion exchange columns operating under non-equilibrium conditions.

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