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Removal of Ammonium from RO Permeate of Anaerobically Digested Wastewater by Natural Zeolite

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Abstract: The purpose of this paper was to study simultaneous removal of ammonia and potassium retained in wastewater by ion exchange with original and sodium conditioned zeolite after membrane treatment of anaerobically digested cattle manure effluents. Batch and column flow-through ion exchange tests were conducted to determine ion exchange capacity, pH effect, exchange kinetics, column runs and regeneration conditions. The exchange capacity of ammonium by original and sodium zeolite, according to the Langmuir equation, was 1.03 ± 0.11 and 1.14 ± 0.050 mmol/g, respectively. The kinetic experiments showed that the sorption of ammonium with coexisting K^+ was rapid at the first 10 min, and approached equilibrium in 1 h. Ammonium removal was stable from lower pH to 9 and significantly decreased at $pH > 10$, while potassium removal was slightly increased at $pH > 10$. Column tests at a flow rate of 8.6–9.8 BV/h with a feed water containing 270 ppm of NH_4^+-N and 200 ppm of K^+ showed that the total exchange capacity was approximately 8.8 mg/g for NH_4^+-N and

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8.3 mg/g for K^+. Both batch and column tests confirmed that zeolite had higher selectivity with potassium than with ammonium. On-column regeneration experiments showed that the exhausted zeolite could be efficiently regenerated by 5 BV brine solution containing 50 g/L NaCl and 0.2 M NaOH. The regenerated zeolite could be further reused for ammonium and potassium removal.

Keywords: Zeolite, anaerobically digested wastewater, removal, ammonia, ion exchange

INTRODUCTION

Concerns over the environment and rising costs for energy and for wastewater treatment have caused a resurgent interest in anaerobic treatment of organic wastes. Anaerobic digestion of animal manure and the corresponding nutrient recovery in the livestock industry can help generate bio-energy, diminish the disposal and odor of wastes, provide the bio-based fertilizer, and greatly minimize negative environmental impacts. One of the effective technologies for treating anaerobically digested effluents is membrane filtration. After the membrane treatment of digested animal manure, a higher level of ammonium along with several other ions still remained in the effluent. The residual ammonia should cause eutrophication, dissolved oxygen depletion, and fish toxicity in receiving water if it is directly discharged. The removal and recovery of the residual ammonia will have both significant environmental and economic benefits.

Residual ammonium in the wastewater can be removed by ion exchange (IE) using natural zeolites. Zeolite is an inorganic porous material having a highly regular structure of pores and chambers and valuable cationic exchange capacity. Natural zeolite has been broadly investigated for this purpose due to its high ammonium ion selectivity. A variety of ammonium-containing wastewaters were used in these studies, including mostly aqueous NH_4Cl solution (1–10), municipal wastewater (3, 11, 12), aquaculture wastewater (13), compost or landfill leachate (9, 14), and animal manure effluents (3, 15).

In municipal or agricultural wastewaters, other cations including Na^+, K^+, Ca^{2+}, and Mg^{2+} are typically co-existent with NH_4^+. Their selectivity of ion-exchange on clinoptilolite was determined by Ames (16) in an order of $K^+ > NH_4^+ > Na^+ > Ca^{2+} > Mg^{2+}$. The presence of these competing cations could affect NH_4^+ uptake on clinoptilolite (1, 5, 8, 9, 11, 13, 17, 18). McVeigh and Weatherle (18) found that among those four competing cations, K^+ showed a highest inhibitory effect on NH_4^+ uptake. Although different ammonium-exchange capacities under the influence of those competing cations have been measured by the above mentioned researchers, but so far no information is available for simultaneous uptake of NH_4^+ and K^+ on clinoptilolite, particularly for the RO permeate with high concentrations of NH_4^+ and K^+.

The aim of this study was to explore a simultaneous uptake of ammonium and potassium on the original and sodium-conditioned zeolite from RO permeate of anaerobically digested cattle manure effluents. The uptake capacities, ion-exchange kinetics, and pH effects were preliminarily evaluated in batch jar tests by using NH_4^+ and K^+ containing RO permeate. The column flow-through ion exchange tests with on-column regeneration were also conducted to determine the breakthrough curves and regeneration efficiencies. This work can provide a further understanding of ammonium removal under the influence of potassium by clinoptilolite.

MATERIALS AND EXPERIMENTAL METHODS

Zeolite and Feed Water

The natural zeolite used in experiments was mined at Idaho, USA. It has an approximately 95% clinoptilolite content, with a general formula of $(Na, K, Ca)_{2\text{-}3}Al_3(Al, Si)_2Si_{13}O \cdot 12H_2O$. Original zeolite contains approximately 3.5% potassium, 1.6% calcium, and less than 0.5% sodium in a grain size of 0.25–2.36 mm. Its cation exchange capacity (CEC) is about 160 to 180 meq/100 grams (from the product descriptions). The sodium-formed zeolite (Na-zeolite) was prepared by using 22.5 bed volumes of 20 g/L NaCl flowing up through the original zeolite fixed bed with a feed rate of 3.2 BV/h, washed with deionized water, and subsequently dried at 105°C.

Real wastewater produced from the membrane treatment of anaerobically digested cattle manure effluents contained approximately 250 mg/L of NH_4^+ and 200 mg/L of K^+ with pH 9.1 and a turbidity <0.1 NTU. Its average composition is shown in Table 1. The synthetic wastewater had similar ion concentrations as the real anaerobically digested wastewater. For batch isothermal

Table 1. Average ion concentrations in RO permeate

Item	Unit	Value
Na^+	mg/L	55
NH_4^+-N	mg/L	250
K^+	mg/L	200
Mg^{2+}	mg/L	0.2
Ca^{2+}	mg/L	0.6
Cl^-	mg/L	110
NO_2^-	mg/L	0
NO_3^-	mg/L	0
PO_4^{3-}	mg/L	0
SO_4^{2-}	mg/L	3

experiments, NH_4^+ or K^+ solutions were separately prepared by dissolving NH_4Cl powder (BDH, Analytical reagent, 99.5% min) or KCl (BDH, Analytical reagent, 99.5% min) in deionized (DI) water.

Determination of Ion Exchange Capacities

Ion exchange capacities for NH_4^+ were determined in isothermal experiments. In a series of 250-ml Erlenmeyer flasks, 50 ml of ammonium (100–600 mg/L) solutions and 1.00 g zeolite were added. The flasks were capped and placed on an orbital shaker at 150 rpm and room temperature (20–21°C) for 18 h. The solution pH was adjusted and settled at 9.0 with 1 mol/L of diluted HCl or NaOH solutions. At the end of the reaction period, the suspension in each flask was filtered through a 0.45-μm membrane filter and the filtrate was analyzed for NH_4^+. The quantity of NH_4^+ uptake by the original and Na-formed zeolite was calculated by the difference of the initial and the final concentration of ions. The duplicate experiments demonstrated the high repeatability of this procedure and the experimental error could be controlled within 5–10%.

For calculation of individual ion exchange capacity, the experimental data were fitted with Langmuir isotherm model expressed as:

$$q_{eq} = \frac{bQ_{max}\, C_{eq}}{1 + bC_{eq}} \tag{1}$$

where Q_{max} (mg/g) is the maximum uptake capacity, C_{eq} (mg/L) is the equilibrium solute concentration, and b is the equilibrium constant related to the energy of sorption (L/mg).

The pH Effects

Experiments for evaluating pH effects followed a similar procedure as for the isothermal experiments. For the original zeolite, a RO permeate solution containing both NH_4^+ and K^+ (approximately 250 mg NH_4^+/L and 200 mg K^+/L) was used while maintaining pH at different values between 4 and 11.5. For the Na-treated zeolite, the solution was prepared using deionized water spiked with 12 mmol/L of NH_4^+ and K^+, respectively.

Simultaneous Uptake Kinetics

In a 1000-mL two-neck distilling flask, 500 mL of RO permeate solution and 20 g of raw and Na-treated zeolite were added. The flask was placed in a water bath and mechanically stirred at 200 rpm. The pH of the solution was adjusted to a constant value near 9.0 with dilute HCl or NaOH solutions and the temperature was maintained at 20 ± 0.5°C. Aliquots of sample solution (1 mL) were withdrawn at various time intervals between 0 and 2 h. The suspension was immediately filtered through a 0.45-μm membrane filter, and the filtrate was analyzed for NH_4^+ and K^+ concentration. The pseudo-second-order kinetic model was used to fit the uptake kinetics of NH_4^+ and K^+. The kinetic rate equation is expressed as:

$$\frac{dq_t}{d_t} = K_2(q_{eq} - q_t)^2 \tag{2}$$

where q_{eq} is the sorption capacity at equilibrium and q_t is the solid-phase loading of ammonium at time *t*. K_2 ($g \cdot mmol^{-1} \cdot h^{-1}$) represents the pseudo-second-order rate constant for the kinetic model. By integrating Equation (2) with the boundary conditions of $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the following linear equation can be obtained:

$$\frac{t}{q_t} = \frac{1}{V_0} + \frac{1}{q_{eq}}t \tag{3}$$

$$V_0 = K_2 \cdot q_{eq}^2 \tag{4}$$

where V_0 ($mmol \cdot g^{-1} \cdot h^{-1}$) is the initial sorption rate. Therefore, the V_0 and q_{eq} values of the kinetic tests can be determined experimentally by plotting t/q_t versus *t*.

Column Flow-through Experiments

Column flow-through tests were conducted at room temperature with RO permeate solutions to determine ammonium and potassium removal capacities. The column made of transparent Plexiglas had an internal diameter of 2.54 cm and a packed height of 28 cm. The RO permeate was continuously pumped from a storage tank to the column downward at a flow rate of 8.6–9.8 BV (bed volume)/h with a calibrated Master flex pump. The estimated flow space-velocity in the column was 4.0–4.6 cm/min. The effluent from the column was sampled for NH_4^+ and K^+ analyses. After each column test, the exhausted zeolite was regenerated on column. The regenerant solution containing 50 g/L of NaCl and 0.2 N of NaOH flew upward through the fixed bed of zeolite at a flow rate of 2.5–3.3 BV/h for about 2.5 h. After that, the column was washed with 1.2–1.4 BV of 0.2 N HCl and 1 BV of DI water to obtain a near neutral pH, and then reused for the next cycle of ammonium and potassium uptake.

Analytical Methods

The NH_4^+ and K^+ concentrations of liquid samples were measured by an ion chromatograph (Dionex ICS-1000).

RESULTS AND DISCUSSION

Ammonium Adsorption Isotherms

To investigate the adsorption capacity of ammonium by zeolite, ammonium adsorption isotherms were drawn and are shown in Fig. 1. NH_4^+ uptake capacities significantly increased with its equilibrium concentration from 0 to 15 mmol/L. With a further increase of the NH_4^+ equilibrium concentration, the increase of the uptake capacity was less significant. The Langmuir isotherm was used to fit the experimental data and the maximum uptake capacities of NH_4^+ can be obtained from the fitting results. The calculated maximum uptake capacities (Q_{max}), the Langmuir sorption constants (b) and the correlation coefficients (r^2) for NH_4^+ are all shown in Table 2. High correlation coefficients ($R^2 > 0.97$) suggested that Langmuir is suitable for describing the uptake equilibrium of ammonium and potassium by clinoptilolite. Q_{max}, the maximum value of q_{eq}, is the most important parameter to identify the adsorption capacity. Determined from Langmuir equation, the maximum adsorption capacity for ammonium by the original and Na-treated zeolite were 1.03 ± 0.11 and 1.14 ± 0.05 mmol/g, respectively. It indicated that the maximum adsorption capacity for ammonium was relatively improved when the zeolite was transferred to Na form from

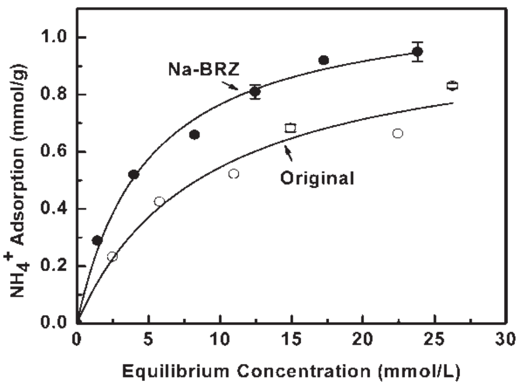

Figure 1. Adsorption isotherms for ammonium by the original and Na-treated zeolite. (temperature 20 ± 1°C, pH 9.0 ± 0.1, and liquid/solids: 50 mL/1 mg).

Table 2. Langmuir adsorption isotherms parameters for ammonium by the different source zeolite

Zeolite type	Q_{max} (mmol NH_4/g)	b (L/mmol)	R^2
Original	1.03 ± 0.11	0.11 ± 0.03	0.97
Na-treated	1.14 ± 0.05	0.203 ± 0.028	0.99

K, Ca, Na-mixed form. The reported maximum ammonium uptake capacities on a variety of clinoptilolite ranged from 0.3 to 1.1 meq/g (3). The current ammonium Q_{max} value was at the high end of the reported range. The ammonium exchange capacity was reported to be 1.5–2 mmol/g for polymeric exchangers at the optimum pH (7, 19) and 1–2 mmol/g for synthetic zeolite (20). However, natural zeolite should be more cost-effective since it is much cheaper than the polymeric exchangers and synthetic zeolite, although inferior to the latter in the adsorption capacity of ammonium.

Kinetics of Ammonium Removal

The kinetics of sorption that describes the solute uptake rate governing the residence time of the sorption reaction is one of the important characteristics, which define the efficiency of adsorption. Figure 2 shows the adsorption of ammonium by original (A) and Na-treated (B) zeolite at different time intervals. The values of V_0, K_2, and q_{eq}, listed in Table 3, were obtained through fitting data in Fig. 2 with the Eqs. (3) and (4). The coefficient of determination $R > 0.997$ indidated that the model fits the experimental data very well. K_2 ($g \cdot mmol^{-1} \cdot h^{-1}$) represents the pseudo-second-order rate constant for the kinetic model.

The ion exchange of ammonium with two zeolites was found to be time dependent (Fig. 2). For both zeolites, ion exchange of ammonium was rapid at the first 15 min and then slowed down considerably, the ammonium exchange approached equilibrium in 60 min. The rate constant (K_2) of ammonium adsorption by Na-treated zeolite was shown as 58.6 $g \cdot mmol^{-1} \cdot h^{-1}$, which was significantly higher than the 38.3 $g \cdot mmol^{-1} \cdot h^{-1}$ from the original zeolite. The initial ammonium adsorption rate (V_0) on Na-treated zeolite increased more than 2 times compared with the untreated zeolite. Both increases of rate constant (K_2) and the initial adsorption rate (V_0) confirmed that the kinetics of ammonium adsorption was preferred while the zeolite was pretreated with sodium ion. Based on the pseudo-second-order kinetic model, the equilibrium adsorption for NH_4^+ by the two zeolites were 0.231

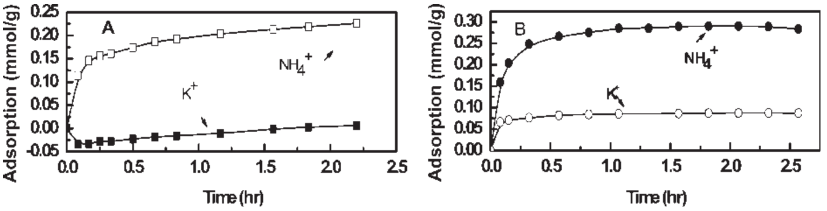

Figure 2. Kinetics of adsorption for ammonium and co-existing potassium by the original (A) and Na-treated (B) zeolite. (Temperature 20 ± 1°C, liquid/solids: 50 mL/1 mg, pH 9.0 ± 0.1, solution background, A: RO permeate, 227 mg NH_4^+-N/L and 198 mg K^+/L, B: deionized water, 236 mg NH_4^+-N/L and 205 mg K^+/L).

and 0.296 mmol/g, respectively. These results were consistent with the results obtained from the adsorption isotherms that ammonium equilibrium adsorption capacity by Na-treated zeolite was evidently higher than that of the original zeolite. Correspondingly, the equilibrium removal efficiency of ammonium by the Na-treated zeolite was 71%, which was significantly higher than 56% of removal by the untreated zeolite. A higher efficiency of ammonium removal by the Na-treated zeolite was probably attributed to the high exchange potential of sodium exchange with ammonium.

The behavior of potassium was different from ammnonium Fig. 3. It was observed that in the first 5 minutes of reaction for the original zeolite, potassium concentration in the supernatant was significantly higher than the initial concentration of potassium. This indicated that the potassium contained in the original zelite was firstly released into the solution. Afterwards, the potassium began to be adsorbed onto the zeolite till the equilibrium concentration of potassium was close to the initial concentration. Compared with insignificant uptake of potassium by the original zeolite, the rate of K^+ uptake by Na-treated zeolite was fast in the initial 5 min and approached equilibrium within 10 min and the equilibrium adsorption reached 0.11 mmol/g. The initial adsorption rate (V_0) for ammonium was higher than for potassium because the initial molar concentration of ammonium was 3.22 times higher than that of potassium. On the other hand, the uptake rate

Table 3. Parameters of a pseudo-second-order kinetic model fitting ammonium adsorption kinetics

Zeolite forms	V_0 $(\mathrm{mmol} \cdot \mathrm{g}^{-1} \cdot \mathrm{h}^{-1})$	q_{eq} (mmol/g)	K_2 $(\mathrm{g} \cdot \mathrm{mmol}^{-1} \cdot \mathrm{h}^{-1})$	R
Original	2.04	0.231	38.3	0.997
Na-treated	5.13	0.296	58.6	0.999
Na-treated	2.71[a]	0.111	219	0.999

[a] K^+

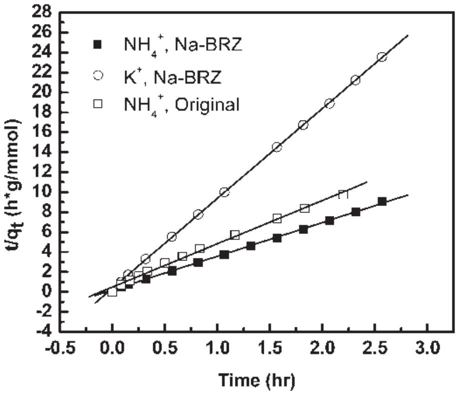

Figure 3. Using pseudo-second-order kinetic model to fit kinetics of adsorption for ammonium and co-existing potassium by the zeolite. (Transformation with t and t/q_t).

constant (K_2) for potassium by Na-zeolite reached $219\,g \cdot mmol^{-1} \cdot h^{-1}$, which was much higher than that for ammonium. The equilibrium NH_4^+/K^+ uptake ratio was 2.67 while the NH_4^+/K^+ ratio was 3.22 in the starting water. This result confirmed that zeolite had a higher selectivity for potassium than for ammonium. The higher exchange selectivity of potassium over ammonium on clinoptilolite is likely attributed to the clinoptilolite crystalline structure, on which potassium can be fixed by coordinating with six framework oxygen atoms (21).

Effects of pH on the Ion Exchange of Ammonium

The pH of the aqueous solution is an important variable that influences ion exchange. The effect of pH on the NH_4^+ and K^+ uptake by the original and the Na-treated zeolite for pH between 4 and 12 is presented in Fig. 4. The uptake of both NH_4^+ and K^+ were not dependent on pH in the range of 4 to 8.5. With a further increase of pH, the NH_4^+ uptake capacity tended to decrease. NH_4^+ uptake efficiency reached only 5% and 2% for the original and the Na-treated zeolite respectively at pH 12. The decrease of NH_4^+ uptake for the zeolite at $pH > 9$ is attributed to the formation of ammonia nitrogen at a high pH, since the equilibrium balance between NH_4^+ and NH_3 in the aqueous solution is strongly dependent on pH and temperature. At pH below 7, ammonia nitrogen exists essentially in the NH_4^+ form regardless of temperature. With the pH increase, the amount of NH_3 increases, which is not favourably adsorbed by zeolite due to its nature of zero charge, thereby caused the decrease of NH_4^+ uptake. In contrast, the K^+ uptake capacity slightly increased at $pH > 9$. K^+ is a dissolved ion at the full range of pH, and thus the pH does not have much influence on its uptake by clinoptilolite.

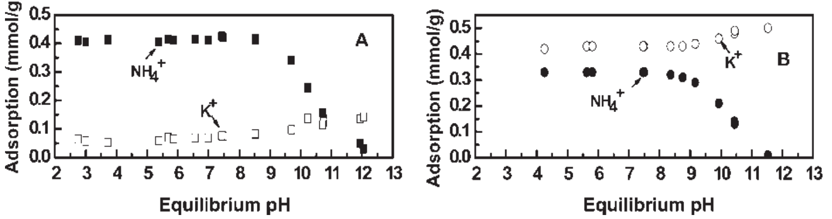

Figure 4. The effect of pH on the adsorption of ammonium and co-existing potassium by the original (A) and Na-treated (B) zeolite. (temperature 20 ± 1°C, pH 9 ± 0.1, liquid/solids: 50 mL/1 mg, solution background, A: RO permeate, 222 mg NH_4^+-N/L and 201 mg K^+/L, B: deionized water, 12 mmol NH_4^+-N/L and 12 mmol K^+/L).

At pH > 9, the increasing K^+ uptake may attribute to the decreased competition from NH_4^+ due to the reduction of the NH_4^+ uptake. The other notification for K^+ was that the uptake of potassium by original zeolite was lower than by Na-treated zeolite at the pH range tested. This was attributed to the conversion of ion type of adsorption sites on zeolite crystal surface.

A similar pH effect on NH_4^+ uptake by clinoptilolite was also observed by Koon and Kaufman (11) and Du et al. (10). Although both showed an uptake maximum at pH 6, an appreciable reduction of uptake capacity with increasing pH is agreeable with the present results. The marginal impact of pH on NH_4^+ and K^+ uptake at pH 9 suggested that ammonium removal from the present RO permeate with a pH value of 9 may not need any pH adjustment. However, pH adjustment is necessary if the polymer exchanger is employed to treat the RO permeate because of its pH sensitivity. But pH adjustment will bring about the operating complexity and increasing costs of operations since the RO permeate has high alkalinity and not easy to be adjusted to an optimum pH 7.

Fixed-bed Column Runs and Recycles

Ammonium breakthrough curves for six recycles are presented in Fig. 5. For the first run by original zeolite, only 8 bed volumes of effluent collected when the ammonium reached the breakthrough point (5 mg N/L). From the breakthrough point (5 BV) to 50 BV, ammonium concentration increased gradually but did not achieve saturation point. This indicated a long mass transfer zone exhibited in the first run by the original zeolite. However, after the first regeneration with sodium, an important observation was the significant improvement of breakthrough point at which effluent increased to 16 BV. And then ammonium concentration in the effluent increased rapidly at the flow volume from 17 to 45 BV. With the further increase of the flow volume,

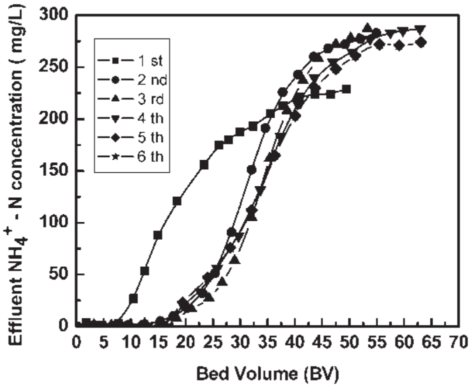

Figure 5. Ammonium breakthrough behavior of the column test from deionized water. (temperature 20 ± 1°C, pH 9 ± 0.1, feed water: RO permeate, 270 mg NH_4^+-N/L and 200 mg K^+/L, inert diameter: 2.54 cm, bed height: 28$\sim$29 cm, SLV: 8.6–9.8 BV/h).

the effluent NH_4^+ concentration approached the influent NH_4^+ concentration and the zeolite column was saturated. Breakthrough curves for the next 5 cycles were nearly identical and most sections overlapped. The improvement of column run efficiency after the first regeneration was attributed to the transformation of zeolite type from (K, Na, Ca,)-mixed form to Na form. It was pointed that sorbed K has a poor exchange potential with ammonium because potassium is located on the site of the crystalline structure of the zeolite with a very low mobility, where it is fixed by coordinating with six framework oxygen atoms. Nevertheless, the sorbed sodium only coordinates with two framework oxygen atoms, which theoretically give the sodium a great facility for ion-exchange (21). The steeper breakthrough curve after the first regeneration is important for the design consideration because it results in a lower critical minimum bed length and decreasing number of columns in series to fully realize the maximum capacity.

The total exchange capacity of ammonium was calculated by numerical integration of the elution profiles, and was presented in Fig. 7. Five regeneration cycles were conducted and no loss of ammonia removal capacity found. The ammonium exchange capacity was increased after the first two regenerations, and then remained constant at the range of 9.0 mg N/g. This indicated that 33–34 BV of RO feed water containing 270 mg N/L of ammonium can be treated if the ammonium removal is conducted in two-column fashion. No loss of ammonium uptake and even a slight increase in its uptake after zeolite regeneration was also observed by Jorgensen et al. (1) and Du et al. (10).

Figure 6 shows potassium flow through histories. The potassium curve of the first run was of significant interest. As seen in the first run, effluent potassium increased very fast from origin to a peak value which was

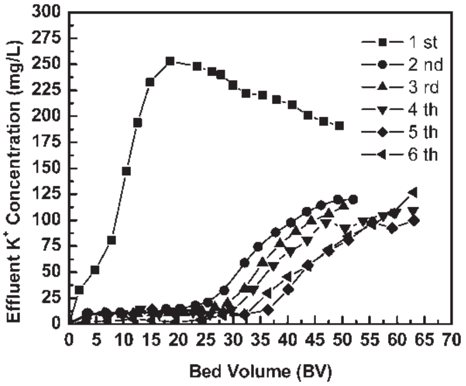

Figure 6. Potassium breakthrough behavior of the column test from deionized water. (temperature 20 ± 1°C, pH 9 ± 0.1, feed water: RO permeate, 270 mg NH_4^+-N/L and 200 mg K^+/L, inert diameter: 2.54 cm, bed height: 28~29 cm, SLV: 8.6–9.8 BV/h).

significantly beyond the influent concentration, and then descent close to (or even below) the initial concentration with time progressed. The flow through curve indicated that potassium experienced three procedures during the first run: potassium uptake, potassium release, and secondly potassium uptake. The special curve of potassium in the first run can be explained by concurrent potassium adsorption and elution during the column run. It was confirmed that the original BRZ was Na, K, Ca mixture-formed zeolite. Potassium adsorption was caused by the ion exchange between liquid K^+ in the RO permeate and solid adsorptive sites of Na^+ and Ca^{2+}, whereas potassium elution was resulted from the ion exchange of ionic NH_4^+ in solution and solid phase K^+ on the original zeolite. First, potassium exhibited to be adsorbed on the zeolite but uptake rate decreased with decreasing available exchange sites of Na^+ and Ca^{2+} on zeolite with time progressed. Afterwards, potassium elution became more and more evident with time elapse, leading to a higher potassium concentration in the effluent than that from the influent in the range of 12–18 BV. With a further increase of time, potassium elution became less significant with the decreasing ion-exchange potential of soluble NH_4^+ ion with fixed K^+, as thus effluent potassium began to be below the influent concentration, and potassium finally showed as a slow uptake process. Overall, the net uptake of potassium in the first run was only 0.58 mg/g. In contrast to the first run, the effluent potassium concentration in the 5 regeneration cycles was very low from the origin to 25–30 BV, and then increased rapidly with time elapse. The curve profiles for 5 regeneration cycles were identical, but the profile front moved forwards with the increase of the cycle time. This indicates that potassium uptake increases with the increase of the uptake-regeneration cycle time.

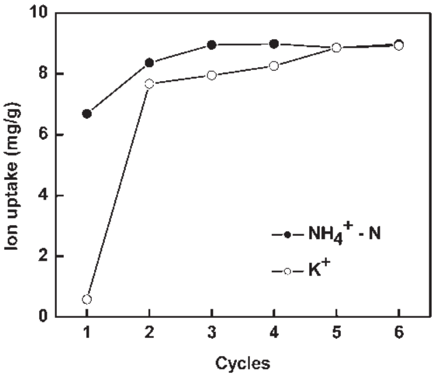

Figure 7. Ammonium and potassium uptake in different cycles of column testing.

The sum of ammonium and potassium uptake by this zeolite in one cycle was on average 0.844 meq/g for five regeneration cycles, in which the molar ratio of the ammonium uptake over the potassium uptake was 3. On the other hand, the molar ratio of ammonium and potassium in the feed water was 3.76. This result further confirmed a higher selectivity for potassium than for ammonium on clinoptilolite. The same conclusion can be made from the observation that the effluent ammonium concentration was slightly higher than that in the influent after the zeolite column reached saturation of ammonium, which was attributed to the displacement of ammonium by potassium during the competition of exchange sites. However, a strong capability of ammonium uptake was realized under column flow-through conditions, even though strong simultaneous uptake of potassium is inevitable.

Regeneration

In order for the sorption process to be viable, zeolite has to be amenable to efficient regeneration and reuse. In the previous articles, pH was usually adjusted to 11.5–12.0 for regenerate the zeolite exhausted (2, 6, 10–12). In those conditions, the highest concentration of ammonia in the regenerant was generally ranged from 250 to 1400 mg/L, and about 15–25 BV brine solution was required to elute out the ammonium absolutely. It was practical using 15–25 BV brine solution to regenerate the exhausted zeolites by the municipal wastewater since more than 100 BV of feed water could be treated while ammonium concentration in feed water was varied from 10 to 70 mg N/L. However, it's not efficient using 15–25 BV brine solution to regenerate the zeolite in this study because only 33∼34 BV RO permeate could be treated. Therefore, it was urgent to decrease the required volume of brine solution by a proper regeneration modification. In this study, the regeneration was realized by backwashing with 0.2 N

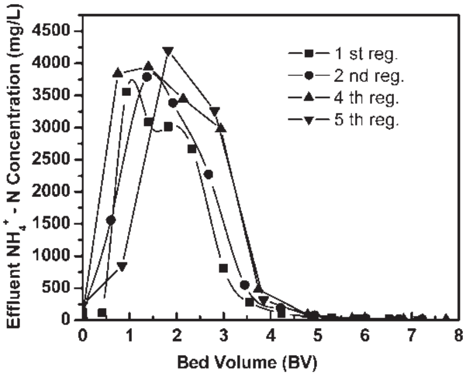

Figure 8. Ammonia eluting curves in the regenerations. (temperature 20 ± 1°C, 0.2 N NaOH & 50 g/L NaCl, 2.5~3.3 BV/h).

NaOH (pH 12.9) & 50 g/L NaCl at 2.5–3.5 BV/h, and followed by 1.2 BV of acid solutions (0.2 N HCl and 50 g/L NaCl) till the effluent pH was near neutral. As seen in Fig. 8, efficient regeneration was obtained using 0.2 N NaOH and 50 g/L NaCl. The highest concentration of ammonia in the regeneration solution reached 4000 mg N/L and 99% of ammonium can be washed out from the saturated zeolite using only 5 BV of the brine solution. A possible circumstance was crystal structure deterioration by increasing alkaline concentration. However, the volume measurment of zeolite indicated only 5 mL of zeolite was lost after 6 recycles, equaling 0.6 percent of volume loss in each reuse.

Compared with a complete elution of ammonium, potassium showed a higher affinity with the zeolite. This can be seen from Fig. 9, the highest

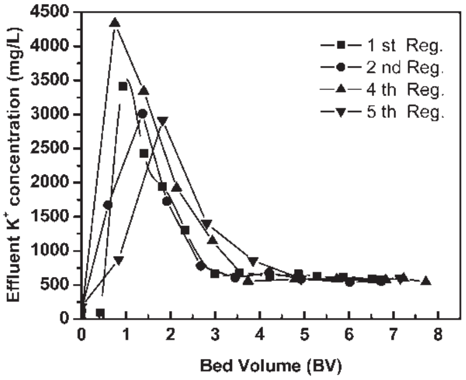

Figure 9. Potassium eluting curves in the regenerations. (temperature 20 ± 1°C, 0.2 N NaOH & 50 g/L NaCl, 2.5~3.3 BV/h).

concentration of potassium in the elution effluent was approximately at 3,000–4,000 mg/L in 5 regeneration cycles, but the potassium was kept stable at a level of 600 mg/L in the range of 4–8 BV, and complete elution never achieved. Regenerant can be reused when ammonium was recovered by steam or air stripping. However, potassium maintained in the refreshed regenerant and increased gradually with the increasing number of reuse times. The effect of accumulated potassium in the regenerant on further ammonium removal efficiency required future investigation.

CONCLUSIONS

The following conclusions can be drawn from the experiments:

1. Ammonium adsorption isotherm by the original and Na-formed zeolite can be fitted well by Langmuir equation, and the exchange capacity of ammonium by original and sodium zeolite were 1.03 ± 0.11 and 1.14 ± 0.05 mmol/g, respectively, indicating an appreciable improvement of adsorption capacity for ammonium when the zeolite was transferred to Na form from the original form.
2. The ion exchange of ammonium with two zeolites was found to be very fast. The reaction was rapid at the first 15 min and then slowed down considerably, the ammonium exchange approached equilibrium in 1 h.
3. The uptake of both NH_4^+ and K^+ were independent on pH between 4 and 8.5, and tended to decrease and more significantly at $pH > 9$. The marginal impact of pH on NH_4^+ and K^+ uptake at pH 9 suggested that ammonium removal from the present RO permeate with a pH value of 9 does not need a pH adjustment.
4. Compared with the original zeolite, the column run efficiency was significantly improved after the first regeneration because of the conversion of zeolite type. After the first regeneration, the sum of ammonium and potassium uptake by the zeolite in one cycle was averaged at 0.844 meq/g for the five regeneration cycles.
5. Highly efficient regeneration performance was obtained when the zeolite was eluted with brine solutions containing 0.2 N NaOH and 50 g/L NaCl.

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