



## **REMOVAL OF AMMONIUM AND POTASSIUM FROM RO PERMEATE OF ANAEROBICALLY DIGESTED CATTLE MANURE BY NATURAL ZEOLITE**

**Xuejun Guo, Larry Zeng\*, Xiaomei Li**

Alberta Research Council Inc., P.O. Bag 4000, Vegreville, Alberta T9C 1T4, Canada.  
\*Email: lzeng@arc.ab.ca; Tel: 780-632-8463.

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### **ABSTRACT**

This work studied simultaneous removal of ammonium and potassium ions by ion exchange with the natural zeolite clinoptilolite. Synthetic and real RO permeate used in experiments contained approximately 250 mg  $\text{NH}_4^+$ /L and 200 mg  $\text{K}^+$ /L. The real RO permeate was obtained from membrane treatment of anaerobically digested cattle manure effluents. Batch experiments were conducted to determine ammonium and potassium ion uptake capacities, exchange kinetics, and pH effects. The experimental isotherm data were fitted well with the Langmuir equation. The equilibrium uptake capacity was 1.14 and 0.88 meq/g for ammonium and potassium, respectively. The simultaneous uptake of both ammonium and potassium was rapid but the potassium uptake was faster than that of ammonium. The uptake of both  $\text{NH}_4^+$  and  $\text{K}^+$  was independent of pH in the range of pH 4 – 8.5. With further pH increase over 9, the  $\text{NH}_4^+$  uptake capacity significantly decreased while the  $\text{K}^+$  uptake capacity slightly increased. The column flow-through ion exchange tests with on-column regeneration were also conducted to determine the breakthrough curves and regeneration efficiencies. Both batch and column tests confirmed a higher selectivity for potassium than for ammonium on clinoptilolite. It was also confirmed that ammonium can be efficiently removed by clinoptilolite under the condition of simultaneous uptake of potassium.

**Keywords:** zeolite, clinoptilolite, ammonium removal, potassium, ion exchange, RO permeate.

## INTRODUCTION

Anaerobic digestion of agricultural and municipal wastes has been increasingly applied for biogas production with the demand for renewal energy. After anaerobic digestion, significant amounts of nitrogen, phosphorus and other plant nutrients always remain in the digested effluents, which are valuable resources for plant growth but also pose potential risk of contamination to water bodies if improperly managed. Therefore, effective removal and recovery of nutrients from the digested effluents becomes necessary for pollution control and environmental sustainability. One promising technology for treating anaerobically digested effluents is membrane separation, involving microfiltration (MF)/ultrafiltration (UF) and reverse osmosis (RO). However, certain levels of ammonium with some other ions, particularly potassium, still remains in the RO permeate, which affects the reuse of this RO permeate for livestock operation. A simple, efficient and cost-effective method for further removal of residual ammonium is therefore needed to supplement the membrane separation process of digested manure treatment.

Ammonium can be removed by ion exchange (IE) using zeolites. A natural zeolite Clinoptilolite has been broadly investigated for this purpose due to its high ammonium-ion selectivity. A variety of ammonium-containing wastewaters were used in such studies, including mostly aqueous  $\text{NH}_4\text{Cl}$  solution (Jorgensen et al. 1976; Czárán et al. 1988; Nguyen and Tanner 1998; Cooney et al. 1999; Çelik et al. 2001; Jorgensen and Weatherley 2003; Weatherley and Miladinovic 2004; Hankins et al. 2004; Du et al. 2005), municipal wastewater (Koon and Kaufman 1975; Booker et al. 1996; Nguyen and Tanner 1998), aquaculture wastewater (Dryden and Weatherley 1989), compost or landfill leachate (Liu and Lo 2001; Hankins et al. 2004), and animal manure effluents (Milan et al. 1997; Nguyen and Tanner 1998).

In most municipal or agricultural wastewaters, other cations such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  are typically co-existent with  $\text{NH}_4^+$ . Their selectivity of ion-exchange on clinoptilolite was determined by Ames (1960) in an order of  $\text{K}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$ . The presence of those competing cations could affect  $\text{NH}_4^+$  uptake on clinoptilolite (Koon and Kaufman 1975; Jorgensen et al. 1976; Klieve and Semmens 1980; Dryden and Weatherley 1989; Cooney et al. 1999; Mc Veigh and Weatherle 1999; Weatherley and Miladinovic 2004; Hankins et al. 2004). Mc Veigh and Weatherle (1999) found that among those four competing cations,  $\text{K}^+$  showed a highest inhibitory effect on  $\text{NH}_4^+$  uptake. Although different ammonium-exchange capacities under the influence of those competing cations have been measured by above researchers, so far no information is available for simultaneous uptake of  $\text{NH}_4^+$  and  $\text{K}^+$  on clinoptilolite, particularly for RO permeate with high concentrations of  $\text{NH}_4^+$  and  $\text{K}^+$ .

The aim of this study was to explore simultaneous uptake of ammonium and potassium on clinoptilolite 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  $\text{NH}_4^+$  and  $\text{K}^+$  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 provided 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  $(\text{Na}, \text{K}, \text{Ca})_{2-3}\text{Al}_3(\text{Al}, \text{Si})_2\text{Si}_{13}\text{O}\cdot 12\text{H}_2\text{O}$ . The balance is primarily opaline or non-crystalline silica. Original zeolite contains approximately 3.5% potassium, 1.6% calcium, and less than 0.5% sodium. Its cation exchange capacity (CEC) is about 160 to 180 meq/100 grams. Before used in ion-exchange experiments, the raw zeolite in a grain size of 0.25-2.36 mm was preconditioned with a 20 g/L NaCl solution, washed with deionized water, and subsequently dried at 105°C. Hence the actual zeolite used in the experiments was the Na-form clinoptilolite.

A synthetic and real RO permeate was used separately in batch and column ion exchange experiments. The real RO permeate produced from membrane treatment of anaerobically digested cattle manure effluents originally having a high concentration of ammonium and potassium both in 2500 – 3000

mg/L contained approximately 250 mg/L of  $\text{NH}_4^+$  and 200 mg/L of  $\text{K}^+$  with pH 9.1 and a turbidity < 1 ntu. Its average composition is shown in Table 1. The synthetic RO permeate had similar ion concentrations as the real RO permeate. For batch isothermal experiments,  $\text{NH}_4^+$  or  $\text{K}^+$  solutions were separately prepared by dissolving  $\text{NH}_4\text{Cl}$  powder (BDH, Analytical reagent, 99.5% min) or  $\text{KCl}$  (BDH, Analytical reagent, 99.5% min) in deionized (DI) water.

**Table 1. Average ion concentrations in RO permeate**

Item	Unit	Value
$\text{Na}^+$	mg/L	55
$\text{NH}_4^+$	mg/L	250
$\text{K}^+$	mg/L	200
$\text{Mg}^{2+}$	mg/L	0.2
$\text{Ca}^{2+}$	mg/L	0.6
$\text{Cl}^-$	mg/L	110
$\text{NO}_2^-$	mg/L	0
$\text{NO}_3^-$	mg/L	0
$\text{PO}_4^{3-}$	mg/L	0
$\text{SO}_4^{2-}$	mg/L	3

#### Determination of ion exchange capacities

Ion exchange capacities for  $\text{NH}_4^+$  and  $\text{K}^+$  were determined in batch isothermal experiments with  $\text{NH}_4^+$  or  $\text{K}^+$  solution separately. In a series of 250-ml Erlenmeyer flasks, 50 ml of ammonium (100-600 mg/L) or potassium (200-1600 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 initially adjusted to 9.0 and readjusted to the same value several times during the experiment with diluted HCl or NaOH solutions. At the end of the reaction period, the suspension in each flask was filtered through a 0.45- $\mu\text{m}$  membrane filter and the filtrate was analyzed for  $\text{NH}_4^+$  or  $\text{K}^+$ . The quantity of  $\text{NH}_4^+$  or  $\text{K}^+$  uptake by zeolite was calculated from the decrease of its concentration in solution. The duplicate experiments demonstrated the high repeatability of this batch procedure and the experimental error could be controlled within 5-10%.

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

$$q_{eq} = \frac{bQ_{max} C_{eq}}{1 + bC_{eq}} \quad (1)$$

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

#### Evaluation of pH effects

Experiments for evaluating pH effects followed a similar procedure as for isothermal experiments, except that a RO permeate solution containing both  $\text{NH}_4^+$  and  $\text{K}^+$  (approximately 250 mg  $\text{NH}_4^+$ /L and 200 mg  $\text{K}^+$ /L) was used while maintaining pH at different values between 4 and 11.5.

#### Measurement of simultaneous uptake kinetics

In a 1000-mL two-neck distilling flask, 500 mL of RO permeate solution and 20 g of 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 diluted HCl or NaOH solutions and the temperature was maintained at  $20 \pm 0.5^\circ\text{C}$ . Aliquots of sample solution (1 mL) were withdrawn with an air displacement pipettor at various time intervals between 0 and 2 h. The sampled solution was immediately filtered through a 0.45- $\mu\text{m}$  membrane filter, and the filtrate was taken for  $\text{NH}_4^+$  and  $\text{K}^+$  analyses.

### 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. RO permeate was continuously pumped from a storage tank to the column downward at a flowrate of 8.6 – 9.8 BV (bed volume) /hr with a calibrated Masterflex pump. The estimated flow space-velocity in the column was 4.0 – 4.6 cm/min. The effluent from the column was sampled for  $\text{NH}_4^+$  and  $\text{K}^+$  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 flow upward through the fixed bed of zeolite at a flow rate of 2.5 - 3.3 BV/hr 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  $\text{NH}_4^+$  and  $\text{K}^+$  concentrations of liquid samples were measured by an ion chromatograph (Dionex ICS-1000).

## RESULTS and DISCUSSION

### Equilibrium uptake capacities of $\text{NH}_4^+$ and $\text{K}^+$

The results of the ammonium and potassium uptake isotherm experiments are shown in Figure 1.  $\text{NH}_4^+$  uptake capacities significantly increased with its equilibrium concentration from 0 to 12.4 mmol/L. Similarly,  $\text{K}^+$  uptake capacities considerably increased with its equilibrium concentrations from 0 to 5 mmol/L. With a further increase of the  $\text{NH}_4^+$  or  $\text{K}^+$  equilibrium concentration, the increase of the uptake capacity was less significant. On a basis of the molar concentration,  $\text{K}^+$  was sorbed in larger amounts than  $\text{NH}_4^+$  at a solute equilibrium concentration approximately smaller than 15 mmol/L. Over this concentration,  $\text{NH}_4^+$  was sorbed slightly more than  $\text{K}^+$ .

Those experimental data were fitted to the Langmuir isotherm to determine the maximum uptake capacities of  $\text{NH}_4^+$  and  $\text{K}^+$ . The calculated maximum uptake capacities ( $Q_{\text{max}}$ ) and the Langmuir sorption constants (b) with the correlation coefficients ( $r^2$ ) for  $\text{NH}_4^+$  and  $\text{K}^+$  are all shown in Table 2.  $Q_{\text{max}}$  for ammonium on this zeolite was 1.14 mmol/g (i.e. 14.8 mg  $\text{NH}_4\text{-N/g}$ ). The reported maximum ammonium uptake capacities on a variety of clinoptilolite ranged from 5 to 15 mg  $\text{NH}_4\text{-N/g}$  (i.e. 0.36 to 1.1 meq/g) (Nguyen and Tanner 1998). The current ammonium  $Q_{\text{max}}$  value was at the high end of the reported range. In contrast,  $Q_{\text{max}}$  for potassium on this zeolite was 34.4 mg/g (i.e. 0.88 meq/g). High correlation coefficients ( $r^2 > 0.978$ ) suggested that Langmuir is applicable for describing the uptake equilibrium of ammonium and potassium by clinoptilolite. The fitting curves by the Langmuir isotherm equation are also plotted in Figure 1.

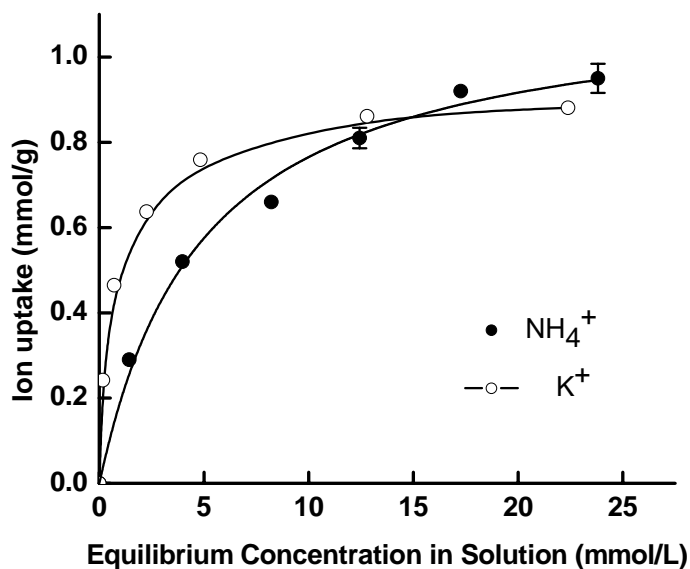


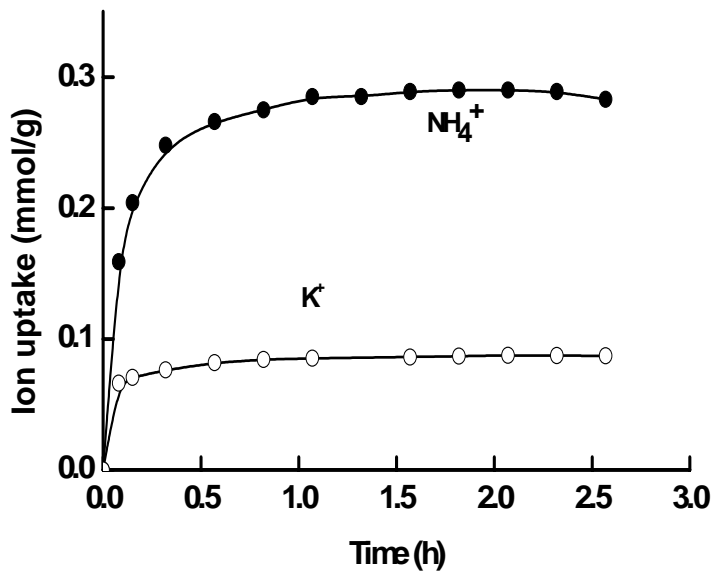
Fig. 1. Uptake isotherms for ammonium and potassium on zeolite at  $20 \pm 1^\circ\text{C}$  and  $\text{pH } 9.0 \pm 0.1$ .

Table 2. Regressed Langmuir isotherm parameters for ammonium and potassium uptake on clinoptilolite.

Ion type	$Q_{\text{max}}$ (mmol/g)	$b$ (L/mmol)	$r^2$
$\text{NH}_4^+$	$1.14 \pm 0.050$	$0.203 \pm 0.028$	0.993
$\text{K}^+$	$0.88 \pm 0.027$	$1.58 \pm 0.250$	0.989

### Kinetics of simultaneous ammonium and potassium uptake

The results of the  $\text{NH}_4^+$  and  $\text{K}^+$  uptake kinetic experiment are shown in Figure 2. The uptake of  $\text{NH}_4^+$  was rapid at the first 15 min and approached equilibrium after approximately 30 min. For example, after 5 and 10 minutes of reaction, the sorbed  $\text{NH}_4^+$  was, respectively, 55% and 70% of that at equilibrium. The rate of  $\text{K}^+$  uptake was even faster in the initial 5 min and approached equilibrium within 10 min. Under the present experimental conditions, the equilibrium uptake efficiencies of ammonium and potassium were 70% and 83%, respectively. Correspondingly, the  $\text{NH}_4^+/\text{K}^+$  molar ratio in solution increased from the initial value 3.22 to 6.13 at equilibrium. This is indicative of a higher selectivity of ion exchange for potassium than for ammonium on clinoptilolite. 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 (Jama and Yücel, 1989). Therefore, the presence of potassium would significantly affect ammonium removal from wastewater by natural zeolite.



**Fig. 2. Kinetics of simultaneous ammonium and potassium uptake at  $20 \pm 1^\circ\text{C}$ ,  $\text{pH } 9.0 \pm 0.1$ , initially  $236 \text{ mg NH}_4^+\text{-N/L}$  and  $205 \text{ mg K}^+\text{/L}$ .**

### Effects of pH on NH<sub>4</sub><sup>+</sup> and K<sup>+</sup> uptake

The pH of the aqueous solution is an important variable that influences ion exchange. The effect of pH on the NH<sub>4</sub><sup>+</sup> and K<sup>+</sup> uptake by this zeolite for pH between 4 and 11.5 is presented in Figure 3. It can be seen that the uptake of both NH<sub>4</sub><sup>+</sup> and K<sup>+</sup> were not dependent on pH between 4 and 8.5. With further increase of pH, the NH<sub>4</sub><sup>+</sup> uptake tended to decrease and more significantly at pH > 9. Its uptake efficiency reached only 2% at pH 11.5. In contrast, the K<sup>+</sup> uptake slightly increased at pH > 9. The effect of pH on NH<sub>4</sub><sup>+</sup> uptake on this zeolite at pH > 9 is most likely attributed to the formation of ammonia nitrogen at a high pH, since the equilibrium between NH<sub>4</sub><sup>+</sup> and NH<sub>3</sub> in the aqueous solution is strongly dependent on pH and temperature (Emerson *et al.* 1975). At pH below 7, ammonia nitrogen exists essentially in the NH<sub>4</sub><sup>+</sup> form regardless of temperature. With the pH increase, the amount of NH<sub>3</sub> increases, which could not be adsorbed by zeolite due to its nature of zero charge, thereby causing the decrease of NH<sub>4</sub><sup>+</sup> uptake. As for K<sup>+</sup>, it is a dissolved ion at the full range of pH, and thus the pH does not have much influence on its uptake by clinoptilolite. At pH > 9, the increased K<sup>+</sup> uptake is evidently attributed to the decreased competition from NH<sub>4</sub><sup>+</sup> due to the reduction of the NH<sub>4</sub><sup>+</sup> uptake.

A similar trend of pH effect on NH<sub>4</sub><sup>+</sup> uptake by clinoptilolite was also observed by Koon and Kaufman (1975) and Du *et al.* (2005). Although both showed an uptake maximum at pH 6, a dramatic reduction of uptake with increase of pH is agreeable with the present results. Interestingly, the present trend of pH effect on NH<sub>4</sub><sup>+</sup> uptake is consistent with that reported by Lin and Lo (1996) using a strong acid cationic ion-exchange resin, in which the NH<sub>4</sub><sup>+</sup> equilibrium exchange capacity remains essentially constant up to pH 7 and decreases fairly rapidly with further increase of pH.

The marginal impact of pH on NH<sub>4</sub><sup>+</sup> and K<sup>+</sup> 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. Another implication from these results is that an acidic condition might be less efficient for exhausted zeolite regeneration, and on the contrast a high pH alkaline solution should be used for recovering ammonium uptake capability during zeolite regeneration.

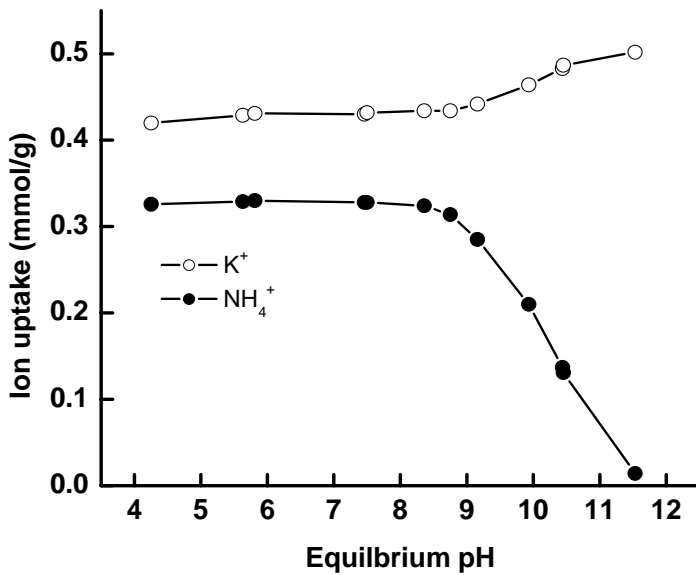
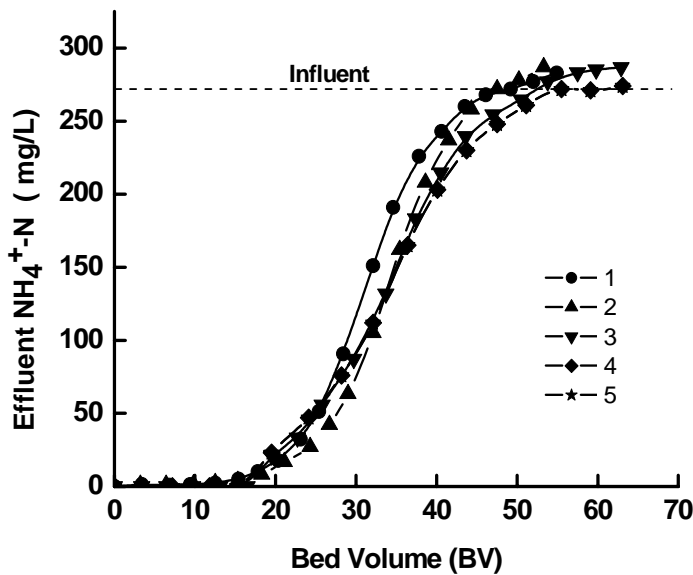


Fig. 3. The effect of pH on ammonium and potassium uptake on clinoptilolite at  $20 \pm 1^\circ\text{C}$ ,  $\text{pH } 9 \pm 0.1$ , initially  $12 \text{ mmol NH}_4^+ \text{-N/L}$  and  $12 \text{ mmol K}^+/\text{L}$ .

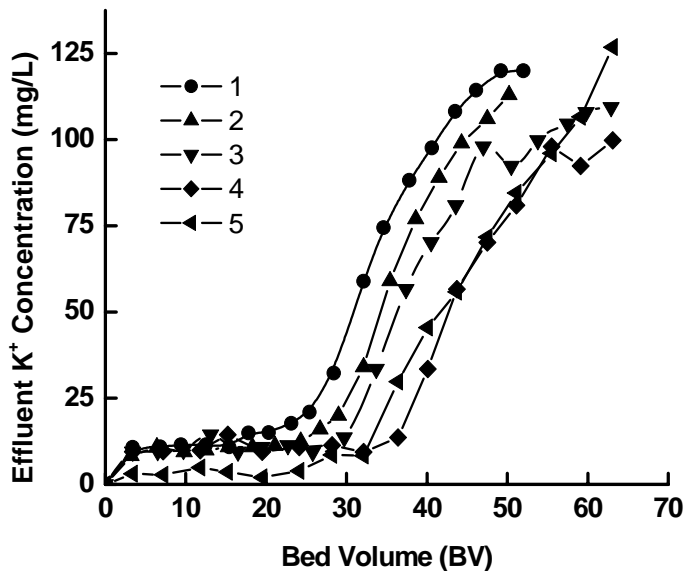
#### Column flow-through tests

The ammonium breakthrough curves of column flow-through tests with  $\text{NH}_4^+$  and  $\text{K}^+$  containing RO permeate from five uptake-regeneration cycles are presented in Figure 4. The breakthrough curves for different cycles were nearly identical and most sections overlapped. The effluent  $\text{NH}_4^+$  concentration was near zero at a flow volume of about 15 BV, within which the ammonium removal efficiency was nearly 100%. Then the ammonium concentration in the effluent increased rapidly at the flow volume from 16 to 45 BV. With further increase of the flow volume, the effluent  $\text{NH}_4^+$  concentration approached the influent  $\text{NH}_4^+$  concentration and the zeolite column was saturated.



**Fig. 4. Ammonium breakthrough curves from five uptake-regeneration cycles with influent 270 mg  $\text{NH}_4^+\text{-N/L}$  and 200 mg  $\text{K}^+\text{/L}$ .**

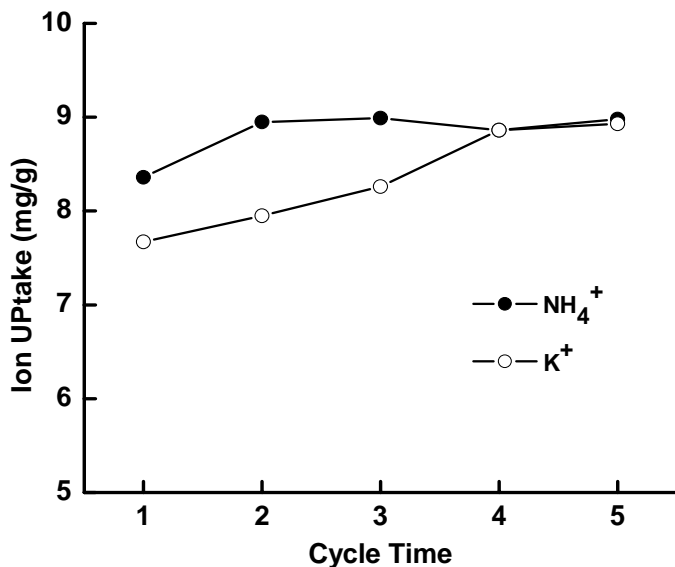
The corresponding potassium breakthrough curves from the column flow-through tests are shown in Figure 5. The curve profiles for different cycles were identical, but the profile front moved forwards with the increase of the cycle time. This means that the potassium uptake increases with the increase of the uptake-regeneration cycle time. The effluent  $\text{K}^+$  concentration never reached zero, but kept a low level at a flow volume of about 25 BV. After that, the potassium concentration in the effluent increased rapidly at the flow volume from approximately 26 to 55 BV. The significant difference between the ammonium and potassium breakthrough curves is that the effluent concentration for potassium does not reach its influent concentration when the one for ammonium does.



**Fig. 5. Potassium breakthrough curves from five uptake-regeneration cycles with influent 270 mg  $\text{NH}_4^+\text{-N/L}$  and 200 mg  $\text{K}^+\text{/L}$ .**

The total uptake of ammonium and potassium in each uptake-regeneration cycle of column flow-through testing obtained from integration of the breakthrough curve is shown in Figure 6. No loss of the ammonium uptake capacity was found during these five cycles of column testing and the actual uptake was slightly increased after the first regeneration, while the potassium uptake capacity was gradually increased with increase of the cycle time. No loss of ammonium uptake and even slight increase in its uptake after zeolite regeneration was also observed by Jorgensen et al. (1976) and Du et al. (2005).





**Fig. 6. Ammonium and potassium uptake in different cycles of column testing.**

The sum of ammonium and potassium uptake by this zeolite in one cycle was 0.844 meq/g on average for these five 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, strong capability of ammonium uptake was realized under column flow-through conditions, even though strong simultaneous uptake of potassium is inevitable.

## CONCLUSIONS

A natural zeolite clinoptilolite from Idaho, USA was tested for simultaneous removal of ammonium and potassium. The following conclusions can be drawn:

- The experimental isotherm data for ammonium and potassium were fitted well with the Langmuir equation. The equilibrium uptake capacity was 1.14 and 0.88 meq/g for ammonium and potassium, respectively.
- The simultaneous uptake of both ammonium and potassium was rapid but the potassium uptake was faster than that of ammonium. Uptake equilibrium was approached in less than 10 and 30 min for potassium and ammonium, respectively.
- The uptake of  $\text{NH}_4^+$  and  $\text{K}^+$  was both independent of pH in the range of pH 4 – 8.5. With a pH increase over 9, the  $\text{NH}_4^+$  uptake significantly decreased, while the  $\text{K}^+$  uptake slightly increased owing to decreased competition from  $\text{NH}_4^+$  at high pH.
- The column flow-through experiments with on-column regeneration showed no loss of the ammonium uptake capacity after zeolite regeneration, while the potassium uptake capacity was gradually increased with the number of the uptake-regeneration cycle.
- Both batch and column tests confirmed a higher selectivity for potassium than for ammonium on clinoptilolite. However, ammonium can be efficiently removed by clinoptilolite under the condition of simultaneous potassium uptake.

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