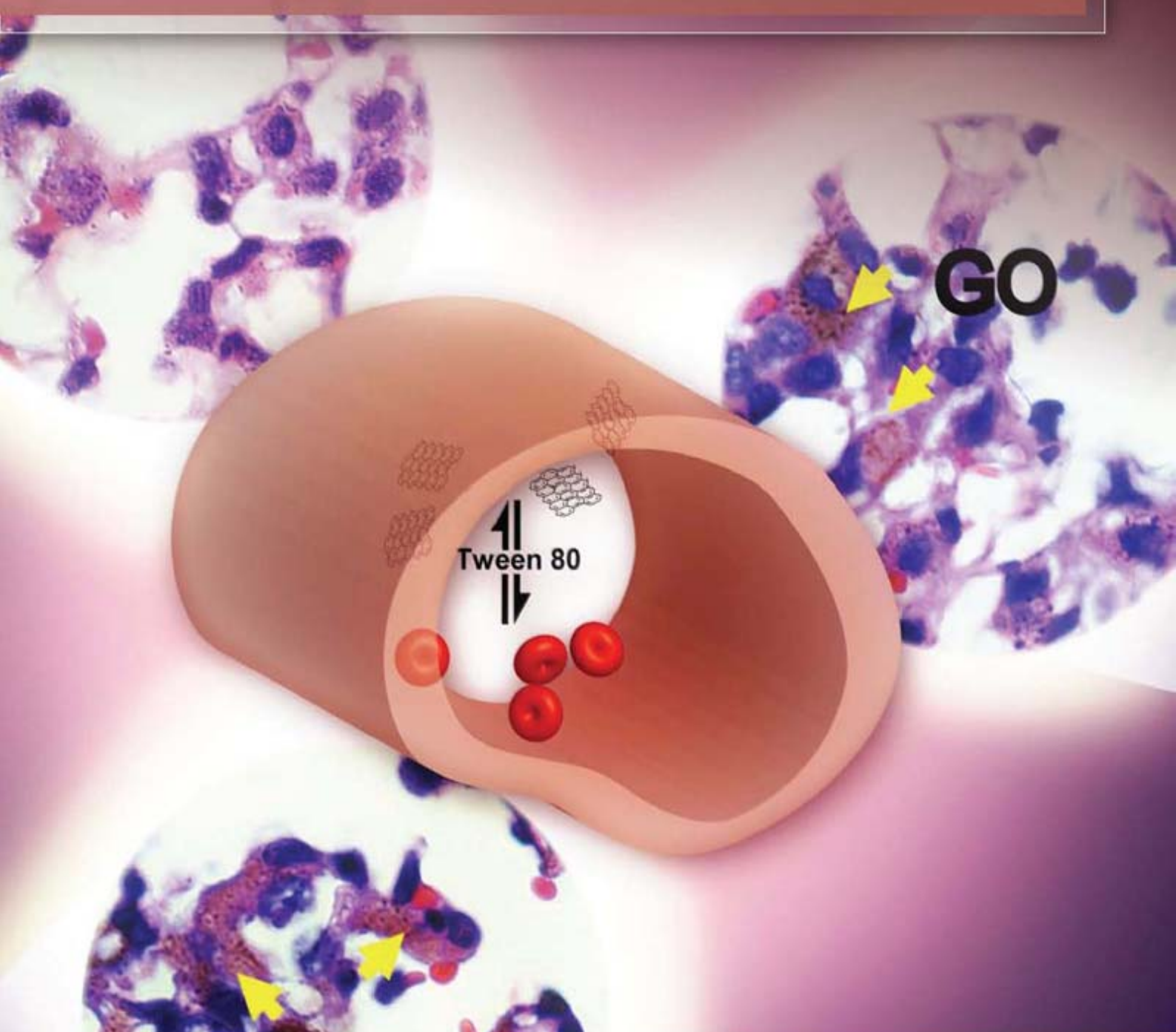


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CONTENTS

Environmental biology

Continuous live cell imaging of cellulose attachment by microbes under anaerobic and thermophilic conditions
using confocal microscopy

Zhi-Wu Wang, Seung-Hwan Lee, James G. Elkins, Yongchao Li, Scott Hamilton-Brehm, Jennifer L. Morrell-Falvey 849

Response of anaerobes to methyl fluoride, 2-bromoethanesulfonate and hydrogen during acetate degradation

Liping Hao, Fan Lü, Lei Li, Liming Shao, Pinjing He 857

Effect of airflow on biodrying of gardening wastes in reactors

F. J. Colomer-Mendoza, L. Herrera-Prats, F. Robles-Martínez, A. Gallardo-Izquierdo, A. B. Piña-Guzmán 865

Environmental health and toxicology

The *ex vivo* and *in vivo* biological performances of graphene oxide and the impact of surfactant on graphene
oxide's biocompatibility (Cover story)

Guangbo Qu, Xiaoyan Wang, Qian Liu, Rui Liu, Nuoya Yin, Juan Ma, Liqun Chen, Jiuyang He, Sijin Liu, Guibin Jiang 873

Determination of the mechanism of photoinduced toxicity of selected metal oxide nanoparticles (ZnO, CuO, Co₃O₄ and
TiO₂) to *E. coli* bacteria

Thabitha P. Dasari¹, Kavitha Pathakoti², Huey-Min Hwang 882

Joint effects of heavy metal binary mixtures on seed germination, root and shoot growth, bacterial bioluminescence,
and gene mutation

In Chul Kong 889

Atmospheric environment

An online monitoring system for atmospheric nitrous acid (HONO) based on stripping coil and ion chromatography

Peng Cheng, Yafang Cheng, Keding Lu, Hang Su, Qiang Yang, Yikan Zou, Yanran Zhao,

Huabing Dong, Limin Zeng, Yuanhang Zhang 895

Formaldehyde concentration and its influencing factors in residential homes after decoration at Hangzhou, China

Min Guo, Xiaoqiang Pei, Feifei Mo, Jianlei Liu, Xueyou Shen 908

Aquatic environment

Flocculating characteristic of activated sludge flocs: Interaction between Al³⁺ and extracellular polymeric substances

Xiaodong Ruan, Lin Li, Junxin Liu 916

Speciation of organic phosphorus in a sediment profile of Lake Taihu II. Molecular species and their depth attenuation

Shiming Ding, Di Xu, Xiuling Bai, Shuchun Yao, Chengxin Fan, Chaosheng Zhang 925

Adsorption of heavy metal ions from aqueous solution by carboxylated cellulose nanocrystals

Xiaolin Yu, Shengrui Tong, Maofa Ge, Lingyan Wu, Junchao Zuo, Changyan Cao, Weiguo Song 933

Synthesis of mesoporous Cu/Mg/Fe layered double hydroxide and its adsorption performance for arsenate in aqueous solutions

Yanwei Guo, Zhiliang Zhu, Yanling Qiu, Jianfu Zhao 944

Advanced regeneration and fixed-bed study of ammonium and potassium removal from anaerobic digested wastewater
by natural zeolite

Xuejun Guo, Larry Zeng, Xin Jin 954

Eutrophication development and its key regulating factors in a water-supply reservoir in North China	
Liping Wang, Lusan Liu, Binghui Zheng	962
Laboratory-scale column study for remediation of TCE-contaminated aquifers using three-section controlled-release potassium permanganate barriers	
Baoling Yuan, Fei Li, Yanmei Chen, Ming-Lai Fu	971
Influence of Chironomid Larvae on oxygen and nitrogen fluxes across the sediment-water interface (Lake Taihu, China)	
Jingge Shang, Lu Zhang, Chengjun Shi, Chengxin Fan	978
Comparison of different phosphate species adsorption by ferric and alum water treatment residuals	
Sijia Gao, Changhui Wang, Yuansheng Pei	986
Removal efficiency of fluoride by novel Mg-Cr-Cl layered double hydroxide by batch process from water	
Sandip Mandal, Swagatika Tripathy, Tapswani Padhi, Manoj Kumar Sahu, Raj Kishore Patel	993
Determining reference conditions for TN, TP, SD and Chl- <i>a</i> in eastern plain ecoregion lakes, China	
Shouliang Huo, Beidou Xi, Jing Su, Fengyu Zan, Qi Chen, Danfeng Ji, Chunzi Ma	1001
Nitrate in shallow groundwater in typical agricultural and forest ecosystems in China, 2004–2010	
Xinyu Zhang, Zhiwei Xu, Xiaomin Sun, Wenyi Dong, Deborah Ballantine	1007
Influential factors of formation kinetics of flocs produced by water treatment coagulants	
Chunde Wu, Lin Wang, Bing Hu, Jian Ye	1015
 Environmental catalysis and materials	
Characterization and performance of Pt/SBA-15 for low-temperature SCR of NO by C ₃ H ₆	
Xinyong Liu, Zhi Jiang, Mingxia Chen, Jianwei Shi, Wenfeng Shangguan, Yasutake Teraoka	1023
Photo-catalytic decolourisation of toxic dye with N-doped titania: A case study with Acid Blue 25	
Dhruba Chakraborty, Susmita Sen Gupta	1034
Pb(II) removal from water using Fe-coated bamboo charcoal with the assistance of microwaves	
Zengsheng Zhang, Xuejiang Wang, Yin Wang, Siqing Xia, Ling Chen, Yalei Zhang, Jianfu Zhao	1044
 Serial parameter: CN 11-2629/X*1989*m*205*en*P*24*2013-5	



Advanced regeneration and fixed-bed study of ammonium and potassium removal from anaerobic digested wastewater by natural zeolite

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Abstract

Highly efficient regeneration of natural zeolite was developed in conjunction with the removal of high concentrations of ammonia and potassium from the reverse osmosis effluent of anaerobic-digested wastewater by fixed-bed ion exchange. The elution and uptake behavior of ammonium and potassium in the fixed bed were studied. Both batch desorption tests and on-column regeneration were conducted to develop an optimum regeneration condition compatible with the wastewater requirements. The effectiveness of ammonium elution increased with increasing alkaline concentration. The increase of salt dose significantly enhanced the ammonium maximum in the elution solution. Complete ammonium elution was achieved in 6 bed volumes (BV) when the alkaline and salt concentrations were respectively 0.1 mol/L and 18.6 g/L at a flow rate of 2.5–3.0 BV/hr. Due to the higher affinity of potassium with natural clinoptilolite, complete potassium elution was not achieved in all cases.

Key words: regeneration; removal; ammonium; potassium; natural zeolite

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Introduction

Concerns over the environment and the rising costs for energy and wastewater treatment have caused a resurgent interest in anaerobic treatment of organic wastes (Fang et al., 2011). Anaerobic digestion of animal manure and the subsequent nutrient recovery can help generate bio-energy, provide bio-based fertilizer, and greatly minimize negative environmental impacts (Astals et al., 2012). Membrane filtration is an effective and growing technology for the treatment of anaerobically digested wastes. After the membrane treatment, a relatively high level of ammonium and several other ions still remain in the effluent. The removal and recovery of the residual ammonia can give significant environmental and economic benefits (Guo et al., 2007, 2008).

Ammonium removal from aquaculture, sewage, municipal and industrial wastewater by natural zeolite was reported in numerous studies, in which the ammonium concentration was usually a few to tens mg/L of NH_4^+ -N (Koon and Kaufman, 1975; Jorgensen et al., 1976; Çelik et al., 2001; Jorgensen and Weatherley, 2003; Weatherley and Miladinovic, 2004; Du et al., 2005; Wei et al., 2011;

Zhang et al., 2011; Wang et al., 2011). There has been increasing application of natural zeolite for ammonium removal with relatively high feed concentration or high ion background (Milan et al., 1997; Hankins et al., 2004; Wang et al., 2006; Liu and Lo, 2001). For anaerobically-digested manure wastewater, the initial NH_4^+ -N may be up to 800–1200 mg/L, along with about 1000 mg/L of K^+ . However, the potential of clinoptilolite for the treatment of anaerobic digestion wastewater, similar to the effluent from the reverse osmosis (RO) of anaerobically-digested effluent containing high concentrations of ammonium (which may reach 250 NH_4^+ -N mg/L) and potassium (200 mg/L), had not been studied in the previous literature.

Zeolite regeneration is generally realized using brine solutions with different brine compositions (Koon and Kaufman, 1975; Dryden and Weatherley 1989; Czrn et al. 1988; Booker et al. 1996; Demir et al., 2002) or by a biological process, where ammonium adsorbed on the zeolite is transferred to gaseous nitrogen species by nitrification-denitrification (Jung et al., 2004). The optimization and improvement of chemical regeneration is of great significance because the regeneration dominates the operational cost of ion exchange by natural zeolite. Koon and Kaufman (1975) investigated the regeneration of clinoptilolite exhausted by municipal wastewater. Dryden and Weatherley

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(1989) studied the regeneration of clinoptilolite after the treatment of aquaculture water. Czrn et al. (1988) concluded that exhausted clinoptilolite could be regenerated more efficiently by potassium ions than by the usually applied sodium ions. As previous studies reported, the ammonium concentration from municipal water (mainly in the range of 10–70 mg/L) was relatively lower than that of manure wastewater. At conditions of high ammonium loading from manure wastewater, it becomes imperative to more efficiently regenerate the exhausted clinoptilolite, and to significantly decrease the required volume of regenerant so as to reach a satisfactory concentration ratio of ammonia between the regeneration solution and the feed water. So far, little information from the literature is available on the uptake and elution behavior of potassium in the ion exchange system with natural zeolite, although the potassium ion is always widely present in this wastewater and significantly influences ammonium removal.

In municipal or agricultural wastewaters, competing ions such as K^+ are typically co-existent with NH_4^+ . The presence of potassium was shown to have a considerable effect on NH_4^+ uptake by clinoptilolite (Cooney, et al., 1999; Weatherley and Miladinovic, 2003; Hankins et al., 2004; Mc Veigh and Weatherley, 1999; Ames, 1960). However, the simultaneous uptake and elution behavior of NH_4^+ and K^+ on clinoptilolite are poorly documented.

The primary objective of this study was to explore conditions under which clinoptilolite may be more effectively regenerated to adapt to the condition of higher ammonium loading from manure wastewater. A batch desorption test was first conducted as a preliminary screen of the regeneration conditions. In on-column regeneration tests, both ammonium and potassium elution efficiencies were investigated in different combinations of alkaline and salt concentrations. The screened regeneration conditions obtained from small scale studies were finally applied in an expanded fixed-bed column.

1 Materials and experimental methods

1.1 Zeolite

The natural zeolite was mined in Idaho, USA. It has an approximately 95% clinoptilolite content, with a general formula of $(Na, K, Ca)_{2-3}Al_3(Al, Si)_{13}O \cdot 12H_2O$. The balance is primarily opaline or non-crystalline silica. The 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 g. Before use, the zeolite in a granular 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.

1.2 Batch desorption tests

A batch desorption test was conducted to investigate the primary desorption behavior of ammonium. Sixty grams

of the zeolite was conditioned with 900 mL of 1000 mg/L ammonium solutions at 150 r/min and room temperature for 15 hr. The pretreated zeolite solid was washed with deionized water several times. Then 1 mL of ammonium saturated zeolite was shaken with 10 mL of different brine combinations at 200 r/min and room temperature for 2 hr. Brine solutions were composed of NaCl ranging from 10 to 93.5 g/L, and NaOH varied between 0.032 and 0.2 mol/L. Subsequently, the ammonium concentration in the supernatant was analyzed to determine the different desorption efficiencies of ammonium in different brine composites. The NH_4^+ and K^+ concentrations of liquid samples were measured by an ion chromatograph (Dionex ICS-1000).

1.3 Column regeneration

In all the column studies, the ion-exchange column was packed with the test zeolite with mass density of 1.03 kg/L. A long column was first saturated with ammonium by pumping synthetic wastewater downward through the column at a flow rate of 10 bed volumes (BV)/hr. Exhausted zeolite was then transferred into a shorter column for a series of regeneration experiments. The short column made of transparent Plexiglas had an internal diameter of 2.54 cm and a packed height of 28 cm. The bed volume was 140 mL. The regenerant solution containing a pre-determined combination of alkaline and sodium chloride flowed upward through the fixed bed at a set flow rate. The ammonium and potassium concentrations in the eluate were analyzed at an appropriate time interval.

1.4 Fixed-bed column run and regeneration application

A synthetic RO permeate was used in fixed-bed column runs. As shown in **Table 1**, the synthetic water had an ionic background similar to the real waste effluent.

Column tests were conducted at room temperature with synthetic wastewater to determine ammonium and potassium removal efficiency. The screened regeneration parameters developed in the smaller column were applied

Table 1 Average ion concentrations in real and synthetic wastewater

Item	Real	Synthetic A	Synthetic B
Na^+ (mg/L)	55	65–70	65–70
NH_4^+ -N (mg/L)	250	270	270
K^+ (mg/L)	200	220–230	220–230
Mg^{2+} (mg/L)	0.2	0.5	15
Ca^{2+} (mg/L)	0.6	5	30
Cl^- (mg/L)	110	110	110
NO_2^- (mg/L)	ND	ND	ND
NO_3^- (mg/L)	ND	ND	ND
PO_4^{3-} (mg/L)	ND	ND	ND
SO_4^{2-} (mg/L)	3	3	3

Real wastewater concentration may vary by $\pm 15\%$; Synthetic A: prepared from distilled water background, column runs No. 1, 2, 4; Synthetic B: prepared from natural water background, column run No. 3. ND: non-detectable.

to a large-scale in-column study. The expanded column had an internal diameter of 10.2 cm and a packed height of 155 cm. Synthetic wastewater was continuously pumped from a storage tank to the column downward at a flow rate of 8–10 BV/hr with a calibrated Masterflex pump. The estimated flow space-velocity in the column was 20–26 cm/min. The effluent from the column was sampled for NH_4^+ , K^+ and other ions analyses. After each column test, the exhausted zeolite was regenerated on-site. The regenerant flowed upward through the fixed bed at a flow rate of 2.5–2.8 BV/hr for about 2.5 hr, and then was neutralized with 1.2–1.4 BV of 0.2 mol/L HCl, and finally washed with 1 BV of clean water before the next cycle of column study.

2 Results and discussion

2.1 Batch desorption of ammonium

The results obtained from batch desorption tests can provide the primary principles of ammonium desorption as a function of alkaline and salt concentration. As seen in **Fig. 1**, at a given concentration of NaCl, the desorption rate of ammonium significantly increased from less than 70% to 90%–95% with alkaline concentration increasing from 0.032 to 0.1 mol/L. However, with a further increase of alkaline concentration, the ammonium desorption remained constant at approximately 90%. At lower alkaline concentration, ammonium desorption was increased with increasing sodium chloride concentration. Specifically, at 0.032 mol/L of alkali, the ammonium desorption rate increased from 53% to 68% with sodium chloride increasing from 10 to 58.5 g/L. Whereas, at 0.1 mol/L or greater alkaline concentration, increasing salt concentration had no significant influence on ammonium desorption when NaCl was up to 20 g/L.

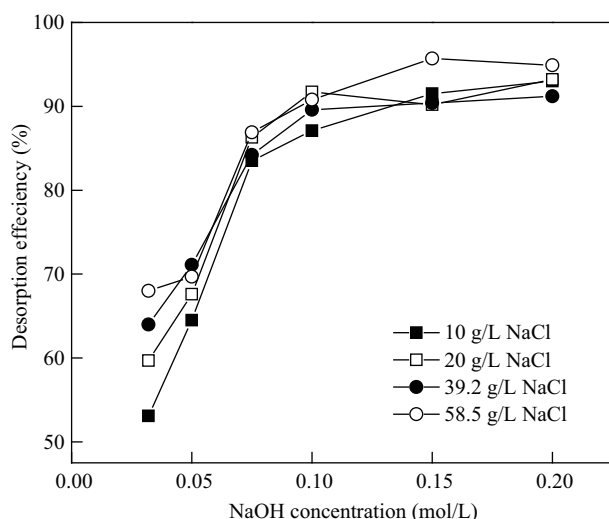


Fig. 1 Ammonium desorption in different alkali and sodium chloride combinations.

2.2 Effect of flow rate

The regeneration efficiency of zeolite was dependent on a few factors, such as alkaline concentration (or pH), salt strength (sodium chloride concentration), and flow rate. The on-column regeneration test was made to determine the dependence of ammonium elution efficiency on the flow rate. The regenerant was composed of 0.1 mol/L of alkali (pH determined as 12.8) and 50 g/L of sodium chloride. **Figure 2** shows the elution curves of ammonia at three different flow rates. The ammonium elution peak was at 1.3 BV with flow rate of 2.8 and 6.2 BV/hr, while it was at 2 BV with flow rate 10.4 BV/hr. The ammonia maximum decreased from approximately 3000 to 2000 $\text{NH}_4^+\text{-N}$ mg/L with the flow rate increasing from 10.4 to 2.8 BV/hr. All of the ammonium was eluted out in 6 BV at 2.8 BV/hr, whereas 10.4 BV regenerant was required at higher flow rates. Koon and Kaufman (1975) found that regenerant flow rates had no significant effect on ammonia elution when the alkaline concentration varied from 7.5×10^{-4} to 5.5×10^{-3} mol/L. The difference of the results between the two studies can likely be ascribed to the different alkaline concentrations employed.

2.3 Combined effect of alkaline and salt strength

Because of the evidence of improved regeneration at lower flow rate, further tests were executed in the range of 2.5–3.0 BV/hr. Elution curves of ammonia at different combinations of alkaline and salt concentration are presented in **Fig. 3**. The elution profile of ammonia can be described on the basis of the ammonium elution maximum and the position where it appeared, and the regenerant volume required for complete ammonium elution. Usually the earlier and higher the ammonium elution peak appeared and the lower the regenerant volume required for complete elution, the higher the effectiveness of regeneration was.

At 0.05 mol/L of alkali, the ammonium maximum was progressively enhanced with increasing salt concentration, at 1300, 3600 and 4900 mg $\text{NH}_4^+\text{-N/L}$ respectively for

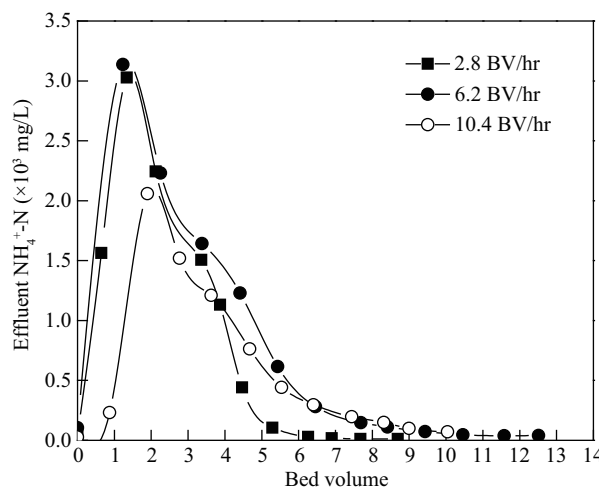


Fig. 2 Ammonium elution curves at different flow rates.

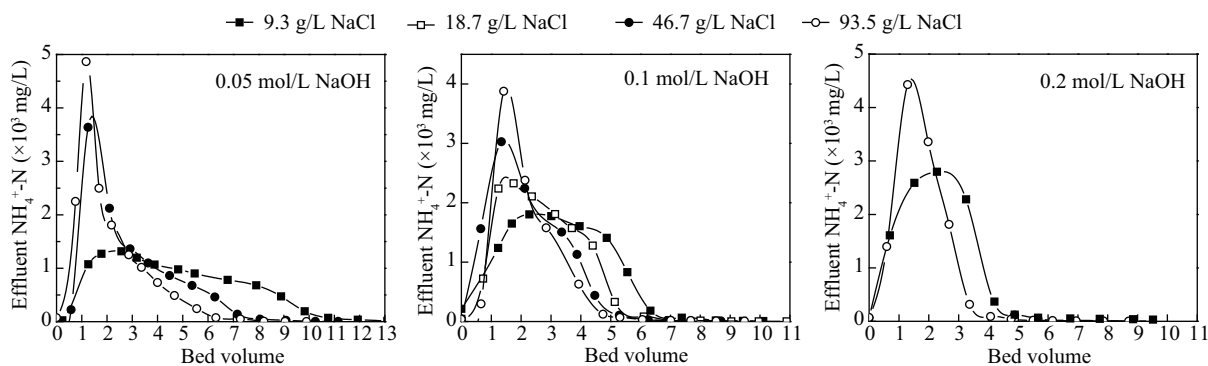


Fig. 3 Ammonium elution curves.

three salt concentrations. Likewise, at 0.1 and 0.2 mol/L of alkali, the ammonium elution peak was significantly enhanced with increasing salt concentration from 9.3 g to 93.5 g/L NaCl. With 9.3 g/L NaCl and alkali from 0.05 to 0.2 mol/L, the ammonia maximum was 1300, 1800, 2800 mg $\text{NH}_4^+\text{-N/L}$ respectively, indicating an appreciable influence of alkali on the ammonium maximum. However, at higher NaCl concentration up to 46.7 mg/L, increasing alkaline concentration had no significant effect on the ammonium maximum. With 46.7 and 93.5 g/L salt strength, ammonium elution peaks appeared at 1.2–1.4 BV for three different alkaline concentrations, whereas at 9.3 g/L of salt, they appeared at 2.3–2.6 BV. This indicated that salt strength potentially influenced the position of the ammonium maximum.

The decisive parameter to evaluate the elution performance of ammonia at a given alkaline and salt concentration is the regenerant volume required for complete elution of ammonium. In most cases in this study, complete ammonium elution was achieved in 10 BV, with the exception of a brine composition of 0.05 mol/L NaOH and 9.3 g/L NaCl. At a given salt concentration, the regenerant required decreased with the increase of alkaline concentration. For example, the regenerant required for complete elution of ammonium was reduced from 11.9 to 5.7 BV with alkali increasing from 0.05 to 0.2 mol/L when the salt strength was 9.3 g/L NaCl.

At 0.05 mol/L of alkali, with salt concentration at 46.7 g/L or greater dose, complete elution of ammonia was

achieved in 8 BV of regenerant. At 0.1 mol/L NaOH, all ammonia was eluted in 6 BV when the salt concentration was 18.7 g/L. Likewise, at 0.2 mol/L NaOH, complete elution was achieved in less than 6 BV even when the salt concentration was 9.3 g/L. These results indicated that at a given alkaline concentration, there existed a certain value of salt concentration to obtain a given regeneration performance; beyond this critical concentration, the further increase of salt concentration would cease to increase the effectiveness of ammonium elution. A similar observation was made by Koon and Kaufman (1975).

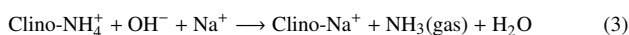
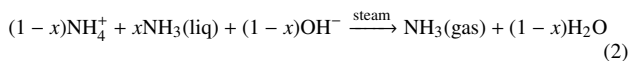
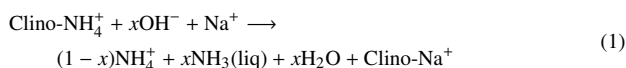
With the goal of achieving higher zeolite regeneration efficiency, the selected alkaline concentration was considerably increased in this study compared with previous reports. Under the new regeneration condition, as illustrated in **Table 2**, the required regenerant volume for complete ammonium elution decreased by 2–4 times relative to the previous literature (Czrn et al., 1988; Demir et al., 2002; Cooney et al., 1999; Du et al., 2005; Koon and Kaufman, 1975; Booker et al., 1996; Dryden and Weatherlay, 1989).

The ammonia retained in the regenerant can be recovered by air or steam stripping and consequently the regenerant can be recycled. The processes of zeolite regeneration and subsequent nutrient recovery by air or steam stripping can be theoretically described by Reactions (1) and (2), respectively ($x \leq 1$). The two processes combined could be described as Reaction (3):

Table 2 Comparison of regeneration parameters and corresponding performance between the previous literature and the current study.

Alkaline strength	Salt concentration (g/L NaCl)	Flow rate (BV/hr)	Ammonia peak (mg $\text{NH}_4^+\text{-N/L}$)	Regenerant required (BV)	Reference
–	–	2	350–500	> 20	Booker et al., 1996
pH 11–12	29	5–10	450	15	Du et al., 2005
pH 12.3	10	16–26	1250–1500	35	Demir et al., 2002
pH 12.3	20	16–26	1250–1500	15	Demir et al., 2002
pH 12	20	10	500	45	Dryden and Weatherlay, 1989
pH 9–11	20–100 (KCl)	2	1200–1400	10	Czrn et al., 1988
pH 10	35	8	700	> 20	Cooney et al., 1999
pH 11.5–12	20–100	10–20	500–1500	15–20	Koon and Kaufman, 1975
pH 12.7 (0.1 mol/L)	20–50	2.5–3.0	2500–4000	6	This study

–: Data not provided in the reference.



Based on Reaction (3), it is shown that the same amount of alkali is required to recover one mole of ammonium from the wastewater when ion exchange and steam (or air) stripping are integrated into the ammonium recovery. If the corrosive effect of alkali on the crystal structure of clinoptilolite is not considered, it is preferable to spike all the required alkali in the first stage ($x = 1$) since higher alkaline concentration resulted in higher regeneration performance. In this study, the ion exchange capacity was about 0.64 mol/L NH_4^+ in the experimental condition. This indicates that 0.64 mole alkali is theoretically required to recover the ion-exchanged ammonium on 1 L saturated zeolite. At concentration of 0.1 mol/L NaOH and 18.7 g/L NaCl (6 BV regenerant is required), the consumed alkali for the regeneration of 1 L zeolite was 0.1×6 mol, very close to 0.64 mol. Thus, 0.1 mol/L alkali was considered as an optimum concentration to regenerate the zeolite. At this alkaline dose, we obtained high efficiency of regeneration as well as complete ammonium recovery. In a case with regenerant spiked with 0.05 mol/L of NaOH, less alkali used in the regeneration stage did not reduce the total alkali use for the integrated process of ammonium removal and recovery, but led to inferior regeneration efficiency.

2.4 Potassium elution

To our knowledge, potassium elution behavior under different regeneration conditions, as displayed in Fig. 4, is comprehensively studied for the first time in this study. At a given salt concentration, the profiles of potassium elution curves were similar in different alkaline concentrations. This indicated that the alkaline concentration had no significant effect on potassium elution. This result was consistent with the initial results obtained from the batch tests,

where pH had no effect on potassium adsorption by clinoptilolite. The potassium elution curve became steeper with increasing salt concentration. The potassium maximum increased significantly with increasing salt concentration, and was below 1000 mg/L at 9.3 g/L NaCl, but up to 4000 mg/L at 93.5 g/L NaCl. Also, the elution efficiency of potassium increased significantly with increasing salt concentration.

In contrast with the ammonium elution curves, complete potassium elution was not achieved in all cases. The incomplete elution of potassium in contrast to ammonium can probably be attributed to the higher affinity of clinoptilolite for potassium and insignificant effect of alkali on potassium desorption. Thus, it can be expected that there was a fraction of adsorption sites that would be occupied by potassium even after the regeneration. Potassium would reduce the performance of ammonium removal, because clinoptilolite has an appreciably higher affinity for potassium than for ammonium. Therefore, it was proposed to conduct the regeneration of zeolite at relatively higher salt concentration to enhance the elution rate of potassium. It was observed that potassium elution was satisfactory when the salt concentration was increased to 46.7 g/L.

2.5 Flow-through runs and regeneration application

The ammonium breakthrough curves of flow-through tests with NH_4^+ and K^+ in simulated wastewater are presented in Fig. 5a. The breakthrough curves for 4 cycles were nearly identical. Two zones were observed for the four breakthrough curves. The first zone was before the breakthrough, where the ammonium concentration in the effluent was near zero for BV < 20. The second was the exponential zone where the ammonium concentration in the effluent increased very fast in the range of 21–45 BV. With further increase of the flow volume, the effluent NH_4^+ concentration approached and even rose beyond the influent NH_4^+ concentration.

The potassium breakthrough curves are shown in Fig. 5b. The curve profiles for different cycles were identical. Overall, the profile had a front moving trend

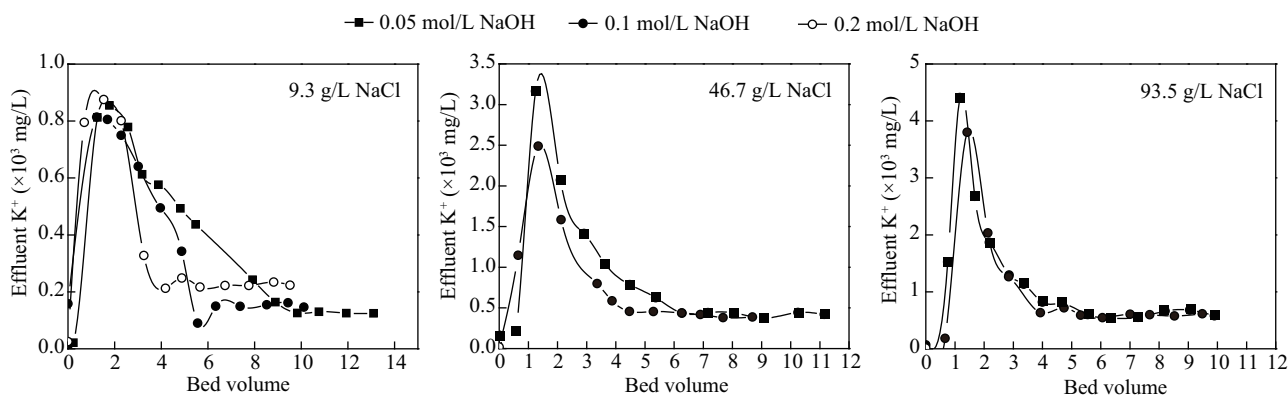


Fig. 4 Potassium elution curves.

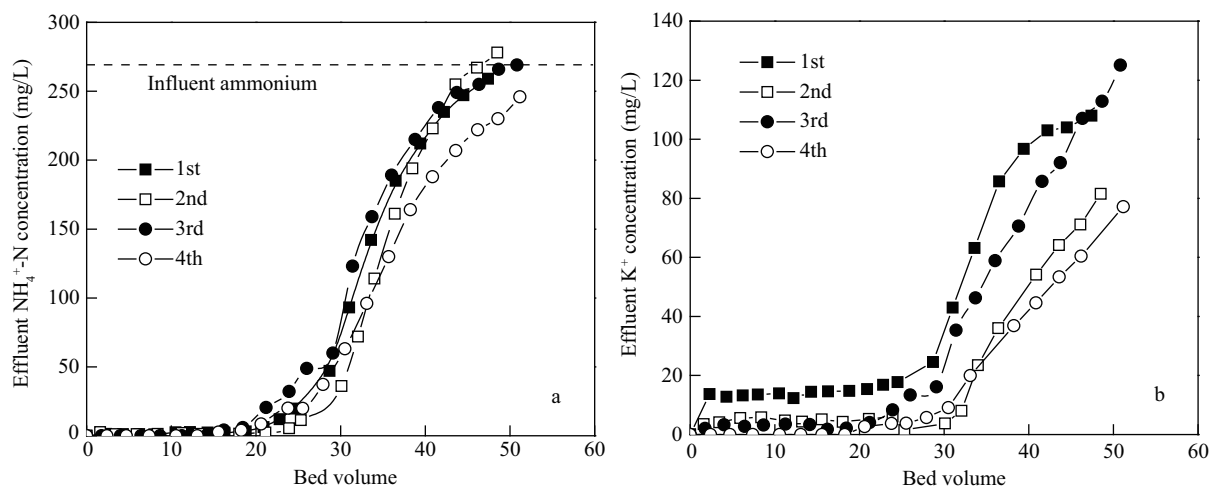


Fig. 5 Breakthrough behaviors of column tests from simulated anaerobically-digested wastewater. (a) NH_4^+ ; (b) K^+ .

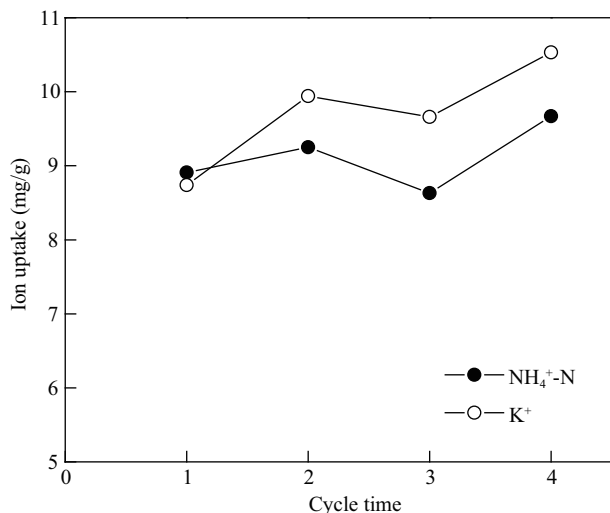


Fig. 6 Ammonium and potassium adsorption in different cycles of column tests.

with the increase of the cycle time. This indicated that the potassium uptake increases with recycling. The effluent K^+ concentration maintained a low level within 30 BV, but increased rapidly from 31 to 55 BV. Effluent K^+ was significantly lower than NH_4^+ , indicating that clinoptilolite had a higher selectivity for K^+ than for NH_4^+ .

The uptake of ammonium and potassium in each cycle of the column test, as shown in Fig. 6, was on average 9.1 and 9.6 mg/g respectively. This indicated that about 35 BV anaerobically-digested wastewater can be successfully treated before the saturation of zeolite. In the four cycles, the molar ratio of the NH_4^+ uptake to the K^+ uptake was 2.6, while its value in the feed water was 3.3. This result further confirmed that the clinoptilolite had a higher selectivity for potassium than for ammonium. Overall, a strong capability of ammonium adsorption was realized, even though strong simultaneous uptake of potassium was inevitable.

Large-scale on-column regeneration experiments were conducted to examine the validity of the regeneration

results. In comparison with the small column of 2.54×28 cm, the expanded column was 10 cm in diameter and 1.55 m bed height. The elution curves of ammonia and potassium from the regeneration of the large column are presented in Fig. 7. Consistent with the results obtained from the small-scale regeneration, complete ammonia elution was achieved within 5–6 BV at brine combination of 0.1 mol/L. Again, complete potassium elution was not achieved.

The post-treatment of zeolite after regeneration with brine solution has rarely been documented in previous studies. Natural zeolite had a tendency to accumulate the alkali in the regenerating operation. It was difficult to wash away the alkali from the column with fresh water alone. Here, the column was flushed with 1.2–1.4 BV of 0.2 mol/L HCl to refresh the ion-exchange column. Previous studies indicated that alkali could affect the crystal structure of clinoptilolite (Koon and Kaufman, 1975). In this study, about 3% mass loss occurred while clinoptilolite was recycled for 7 times. Therefore, the loss of zeolite during regeneration will not be a major concern.

3 Conclusions

On-column regeneration was favored at lower flow rate of 2.5–3.0 BV/hr. Salt strength significantly influenced the ammonium maximum as well as its position. The regeneration efficiency of ammonium was increased with the increase of alkaline concentration. For most cases in this study, complete ammonium elution was achieved in 10 BV. Complete elution of ammonium was achieved in 6 BV of brines when the alkaline and salt concentration was respectively 0.1 mol/L and 18.7 g/L. Potassium elution increased significantly with increasing salt strength, but was negligibly influenced by alkaline variation. About 35 BV of the tested wastewater containing 250 $\text{NH}_4^+\text{-N}$ mg/L could be successfully treated with the tested zeolite. In conclusion, the advanced regeneration of zeolite developed in this study shows promise for application in other ion exchange practices using natural zeolite.

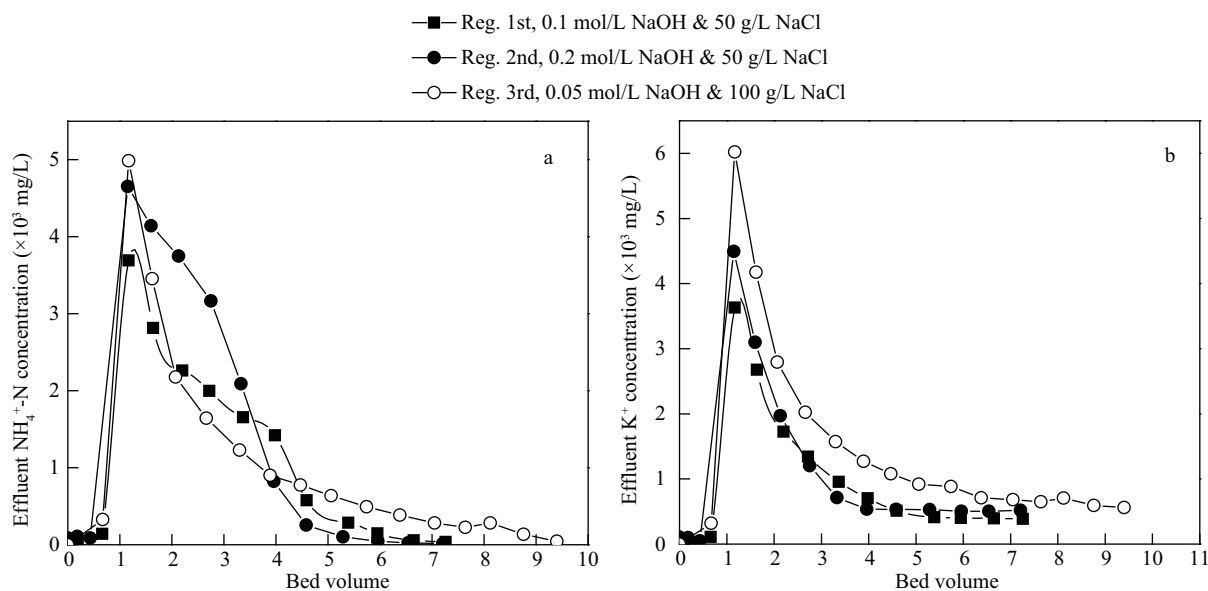


Fig. 7 Elution curves of cations from expanded on-column regeneration. (a) NH_4^+ ; (b) K^+ .

Acknowledgments

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References

- Ames L L, 1960. The cation sieve properties of clinoptilolite. *American Mineralogist*, 45: 689–700.
- Astals S, Nolla-Ardèol V, Mata-Alvarez J, 2012. Anaerobic co-digestion of pig manure and crude glycerol at mesophilic conditions: Biogas and digestate. *Bioresource Technology*, 110: 63–70.
- Booker N A, Cooney E L, Priestley A J, 1996. Ammonia removal from sewage using natural Australian zeolite. *Water Science and Technology*, 34(9): 17–24.
- Çelik M S, Özdemir B, Turan M, Koyuncu I, Atesok G, Sarikaya H Z, 2001. Removal of ammonia by natural clay minerals using fixed and fluidised bed column reactors. *Water Science and Technology: Water Supply*, 1(1): 81–88.
- Cooney E, Booker N A, Shallcross D C, Stevens G W, 1999. Ammonia removal from wastewaters using natural Australian zeolite. II. Pilot-scale study using continuous packed column process. *Separation Science and Technology*, 34(14): 2741–2760.
- Czrn E, Mészros-Kis Á, Domokos E, Papp J, 1988. Separation of ammonia from wastewater using clinoptilolite as ion exchanger. *Nuclear and Chemical Waste Management*, 8(2): 107–113.
- Demir A, Günay A, Debik E, 2002. Ammonium removal from aqueous solution by ion-exchange using packed bed natural zeolite. *Water SA*, 28(3): 329–335.
- Dryden H T, Weatherley L R, 1989. Aquaculture water treatment by ion exchange: continuous ammonium ion removal with clinoptilolite. *Aquacultural Engineering*, 8(2): 109–126.
- Du Q, Liu S, Cao Z, Wang Y, 2005. Ammonia removal from aqueous solution using natural chinese clinoptilolite. *Separation and Purification Technology*, 44(3): 229–234.
- Fang C, Boe K, Angelidak I, 2011. Anaerobic co-digestion of by-products from sugar production with cow manure. *Water Research*, 45(11): 3473–3480.
- Guo X, Zeng L, Li X, Park H S, 2007. Removal of ammonium from RO permeate of anaerobically digested wastewater by natural zeolite. *Separation Science and Technology*, 42: 3169–3185.
- Guo X, Zeng L, Li X, Park H S, 2008. Ammonium and potassium removal for anaerobically digested wastewater using natural clinoptilolite followed by membrane pretreatment. *Journal of Hazardous Materials*, 151: 125–133.
- Hankins N P, Pliankarom S, Hilal N, 2004. Removal of NH_4^+ ion from NH_4Cl solution using clinoptilolite: a dynamic study using a continuous packed-bed column in up-flow mode. *Separation Science and Technology*, 39(6): 1347–1364.
- Jorgensen S E, Libor O, Grabir K L, Barkacs K, 1976. Ammonia removal by use of clinoptilolite. *Water Research*, 10(3): 213–224.
- Jorgensen T C, Weatherley L R, 2003. Ammonia removal from wastewater by ion exchange in the presence of organic contaminants. *Water Research*, 37(8): 1723–1728.
- Jung J Y, Chung Y C, Shin H S, Son D H, 2004. Enhanced ammonia nitrogen removal using consistent biological regeneration and ammonium exchange of zeolite in modified SBR process. *Water Research*, 38(2): 347–354.
- Koon J H, Kaufman W J, 1975. Ammonia removal from municipal wastewaters by ion exchange. *Journal WPCF*, 47(3): 448–465.
- Liu C H, Lo K V, 2001. Ammonia removal from composting leachate using zeolite. I. Characterization of the zeolite. *Journal of Environmental Science and Health A*, 39(9): 1671–1688.
- Mc Veigh R J, Weatherley L R, 1999. Effect of other cations in wastewaters on the ion-exchange removal of ammonium ion. *Dev. Chemical Engineering and Mineral Proceedings*,

- 7: 69–84.
- Milan Z, Sánchez E, Weiland P, Pozas C, Borja R, Mayari R et al., 1997. Ammonia removal from anaerobically treated piggery manure by ion exchange in columns packed with homoionic zeolite. *Journal of Chemical Engineering*, 66(1): 65–71.
- Wang Q H, Yang Y N, Yu C, Huang H, Kim M, Feng C P et al., 2011. Study on a fixed zeolite bioreactor for anaerobic digestion of ammonium-rich swine wastes. *Bioresource Technology*, 102(14): 7064–7068.
- Wang Y, Liu S, Han T, Chuan S, Zhu T, 2006. Ammonia removal from leachate solution using natural Chinese clinoptilolite. *Journal of Hazardous Materials*, 136(3): 735–740.
- Weatherley L R, Miladinovic N D, 2004. Comparison of the ion exchange uptake of ammonium ion onto New Zealand clinoptilolite and mordenite. *Water Research*, 38(20): 4305–4312.
- Wei Y X, Ye Z F, Wang Y L, Ma M G, Li Y F, 2011. Enhanced ammonia nitrogen removal using consistent ammonium exchange of modified zeolite and biological regeneration in a sequencing batch reactor process. *Environmental Technology*, 32(11-12): 1337–1343.
- Zhang M L, Zhang H Y, Xu D, Han L, Niu D X, Zhang L Y et al., 2011. Ammonium removal from aqueous solution by zeolites synthesized from low-calcium and high-calcium fly ashes. *Desalination*, 277(1-2): 46–53.

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