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Removal of Ammonium Ions from Fellmongery Effluent by Zeolite

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ABSTRACT

The introduction of the Resource Management Act in 1991 in New Zealand enforces statutory requirements for the disposal of farm and industrial wastewaters in ways that minimize environmental impacts. Wastewaters often contain high concentrations of ammonium (NH_4^+), phosphate (H_2PO_4^-) and potassium (K^+) ions, and in some cases heavy metals. Zeolite is a naturally occurring, porous and electrically-charged alumino-silicate mineral, which can be used to adsorb cation and anion contaminants from wastewater.

Zeolites of New Zealand origin were obtained from New Zealand Resource Refineries Ltd. and evaluated for their effectiveness to remove

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NH_4^+ ions from a fellmongery wastewater stream. The natural zeolites were of clinoptilolite species and had high cation exchange capacity (CEC) ($> 100 \text{ cmol kg}^{-1}$), which after treatment with alkali solutions increased by up to 74%. The CEC of the zeolites indicated that these samples can hold a potential maximum of 18.7 to 20.1 g NH_4^+ kg^{-1} zeolite.

The adsorption of NH_4^+ ions by the zeolites increased with increasing NH_4^+ ion concentration in the fellmongery wastewater. The presence of other cations in the fellmongery wastewater apparently interfered with NH_4^+ ion adsorption, resulting in only a small fraction of the CEC getting occupied by the NH_4^+ ions. Although an increase in CEC due to alkali treatment increased the adsorption of NH_4^+ ions, H^+ ion saturated zeolites adsorbed higher amount of NH_4^+ ions than the zeolites saturated with other cations. The cation-loaded zeolite was regenerated for NH_4^+ ion adsorption by leaching with 0.5 M HCl, and even after 12 regeneration cycles the amount of NH_4^+ ion adsorption remained unaffected, indicating the potential for recycling zeolite for removing NH_4^+ ions from the waste stream.

Key Words: Ammonium; Cation exchange capacity (CEC); Cation adsorption; Fellmongery; Nutrient ions; Wastewater; Zeolite.

INTRODUCTION

Large quantities of cattle and sheep skins are processed in New Zealand. Fellmongering is the first step in skin processing that involves removal of hair from freshly slaughtered animals followed by pickling of the skin.^[1,2] After initial washing with cold water, the skin is coated with depilatory, usually a lime-sulfide paste that diffuses into the skin and eventually dissolving the hair follicle. The dehaired skin, called pelt, is bathed either in neutralizing acid (boric, acetic or lactic acid) or acidic salt (ammonium chloride, ammonium sulfate or sodium sulfite) solution. Once the pelt is at neutral pH it is enzymatically treated (bated) to remove interfibrillary protein, a step that makes the pelt soft and pliable. The final step in fellmongering is pickling the pelt with sodium or ammonium chloride and sulphuric acid. The pickled pelt, called hide, is sent for tanning.

Fellmongering 1000 sheep skins per day could produce 45 to 60 m^3 of two main wastewater streams called predelime and delime. Predelime wastewater stream results from the first stage of processing in which the skin is treated with lime paste. The delime wastewater stream results from the subsequent neutralizing and pickling treatment. Both wastewater streams are rich in ammonium nitrogen ($\text{NH}_4^+\text{-N}$), which originates from the subcutaneous skin layer during the lime treatment, and/or the treatment chemicals.

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In New Zealand, domestic, farm and industrial wastewaters are often treated biologically using two-pond systems and historically the treated wastewaters are discharged to streams. Biological treatment of wastewater using the two-pond system could achieve a high degree of removal of the biochemical oxygen demand (BOD) and suspended solids in the wastewater, but are not effective in removing nutrients and heavy metals,^[3] which become pollutants when discharged to streams.^[4-6]

With the introduction of the Resource Management Act in 1991 in New Zealand, Regional Councils have focused more attention on water quality. In most regions, discharge of farm and industrial wastewaters to surface waters is now a controlled or a discretionary activity, which requires resource consent.^[7-9] Commonly, resource consent requires wastewater contaminant concentration to be minimized before entering surface water, which can be achieved by land disposal of wastewaters or contaminant-stripping of wastewaters by tertiary treatment.

In New Zealand, the common method of utilizing farm effluents is returning them directly to pasture. Whereas, sewage and industrial wastewaters are often applied to forestry in order to minimize the contaminants reaching the food chain. Many Regional Councils advocates land application of effluents as being less harmful to water resources.^[9] However, land disposal of wastewaters may present some problems that include: (i) encouraged only when the soil moisture and climatic conditions are favorable; (ii) requires greater pond storage facilities for holding effluent when the soil moisture and climatic conditions are unfavorable for land application; (iii) difficult and counter productive when land is waterlogged; (iv) can contaminate groundwater and surface water by leaching and runoff; and (v) the aerosols formed during spraying onto land results in odor problems.

Porous electrically-charged materials can be used to adsorb contaminants from wastewaters,^[10,11] after which they can be discharged safely into waterways or streams. Zeolite is a naturally occurring, porous and electrically-charged alumino-silicate mineral, which can be used to retain cations and anions from wastewaters.^[12-19] The removal of NH_4^+ ions by zeolite, in part depends on the concentration of other cations in the wastewater. It is important that the chemical characteristics of the wastewater are known before attempting to use zeolite to remove NH_4^+ ions from the wastewater. The objectives of this study were to: (i) measure the cation exchange characteristics of zeolite; (ii) examine ways to increase the cation exchange capacity of zeolite; and (iii) examine the removal of NH_4^+ ions from a fellmongery wastewater stream. The ultimate aim of the project was to develop a commercial system that utilizes zeolite to remove NH_4^+ ions from wastewater streams.

MATERIALS AND METHODS

Charge Properties of Zeolite

A number of zeolites representing various deposits in New Zealand were obtained from a local company, New Zealand Resource Refineries Ltd. The samples were air-dried and ground to less than 2 mm fraction. The exchangeable cations and the cation exchange capacity (CEC) were measured by leaching columns containing the zeolites with 1 M NH_4OAc followed by 1 M NaCl .^[20] The concentrations of exchangeable cations (Ca^{2+} , Mg^{2+} , K^{+} and Na^{+}) in the NH_4OAc leachate were measured using an Atomic Absorption Spectrophotometer. The concentration of NH_4^{+} ions in the NaCl leachate was measured using an auto-analyzer.

Increasing CEC of Zeolite

Removal of amorphous materials from zeolite matrix has been shown to enhance its CEC.^[21] Samples II, III and IV were selected to examine the effect of removal of amorphous materials in the zeolite crystal lattices on its CEC. About 50 g of zeolites were boiled for 30 min in 300 mL of 0.5 M NaOH , 0.5 M NaHCO_3 or 0.5 M HCl , and then washed thoroughly with demonized water. These samples were air-dried and ground to ≤ 2 mm size. The CEC of the treated zeolites was measured by leaching with 1 M NH_4OAc as described earlier.

Ammonium Adsorption from Wastewater

Ammonium adsorption by the treated and the untreated zeolites was measured in a column experiment using wastewater from a fellmongery. The concentration of NH_4^{+} ions and other cations in the two wastewater streams collected from the fellmongery is given in Table 1. One hundred g of zeolites were taken in a number of PVC columns (34 mm diameter) and leached with the fellmongery wastewater samples at a flow rate of 4.5 mL min^{-1} . The leachate samples were collected at regular intervals and the concentration of $\text{NH}_4^{+}\text{-N}$ in the leachate measured using an auto-analyzer. Leaching was continued till the concentration of NH_4^{+} ions in the leachate effluent reached that of the influent wastewater. The amount of NH_4^{+} ion adsorbed was estimated from the relationship between the volume of leachate and its NH_4^{+} ion concentration (i.e., breakthrough curve).

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Table 1. Concentration of major cations in the wastewater streams.

Wastewater stream	Concentration (g m ⁻³)				
	NH ₄ ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺
Predelime	715	1380	1.6	1728	23
Delime	1210	972	48.8	1536	38

Regeneration of CEC

The cation exchange sites for NH₄⁺ ion adsorption was regenerated by treating the NH₄⁺ ion-loaded zeolites with 0.5 M HCl. The untreated and acid-treated (to remove amorphous material) zeolites were used for regeneration. The acid-treated sample was used because it retained the highest amount of NH₄⁺ ion. These samples were first leached with the wastewater for NH₄⁺ ion adsorption. After the NH₄⁺ ion adsorption measurement, the columns containing these samples were subsequently leached with 0.5 M HCl over a period of 12 hours. Regeneration with 0.5 M HCl leaching was carried out 12 times and the adsorption of NH₄⁺ ion measured after each regeneration step.

RESULTS AND DISCUSSION**Charge Properties of Zeolite**

The CEC of the zeolites, calculated from the concentration of NH₄⁺ ions in the NaCl leachates after saturating the column with NH₄⁺ ions using 1 M NH₄OAc, ranged from 26 to 112.9 cmol kg⁻¹ (Table 2). Samples III, IV, VI and XI had CEC greater than 100 cmol kg⁻¹. These values are comparable to the values obtained in other studies for different zeolite sources.^[22,23] Most of the cation exchange sites of the natural untreated zeolites were occupied by Ca²⁺ and Na⁺ ions. If all the exchange sites were available for adsorption, the zeolites with CEC > 100 cmol kg⁻¹ could have hold between 18.7 to 20.1 g NH₄⁺-N kg⁻¹ zeolite.

Increasing CEC of Zeolite

Boiling with the alkali and acid solutions resulted in the breakdown of some of the zeolite particles. There was an increase in the amount of fine

Table 2. Exchangeable cations and the CEC of the zeolites.

Sample no	Ca ²⁺ (cmol kg ⁻¹)	Mg ²⁺ (cmol kg ⁻¹)	K ⁺ (cmol kg ⁻¹)	Na ⁺ (cmol kg ⁻¹)	H ⁺ (cmol kg ⁻¹)	CEC (cmol kg ⁻¹)
I	32.8	3.8	15.2	24.5	9.4	85.7
II	24.6	3.5	17.1	29.1	13.1	87.3
III	40.3	4.2	21.6	37.4	9.4	112.9
IV	35.5	3.5	21.6	34.2	9.4	104.3
V	5.6	5.2	12.6	21.5	23.1	67.9
VI	41.8	4.8	17.6	31.4	10.6	106.2
VII	9.5	6.4	20.9	29.6	9.4	75.7
VIII	3.0	3.5	5.6	6.3	7.5	26.0
IX	27.0	7.3	8.2	37.0	7.5	87.0
X	32.2	5.9	15.4	34.2	7.5	95.3
XI	47.6	3.0	23.0	22.1	8.7	104.4

particles (< 0.02 mm) and maximum breakdown occurred in the acid-treated samples. Sample IV produced the highest amount of fine particles after acid treatment causing slow percolation during the CEC measurements. There was a significant increase (almost 70% increases) in the CEC of the alkali-treated zeolite (Table 3). However, acid treatment resulted in only a small increase in the CEC of the zeolites. Curkovic et al.^[21] showed that heating natural zeolite with 2 M NaCl at 70°C increased both the exchange capacity and the efficiency of Cd²⁺ and Pb²⁺ removal from wastewater, which they attributed to the attainment of near homoionic state in Na-form and to the removal of amorphous impurities from the zeolite surface.

Ammonium Adsorption from Wastewater

Ammonium adsorption by the untreated and treated zeolites measured using both the predelime and delime wastewater samples from the fellmongery, ranged from 1.63 to 13.05 g NH₄-N kg⁻¹ zeolite (Table 3). Ammonium adsorption was higher in the latter wastewater (Fig. 1A), which can be attributed to higher concentration of NH₄⁺ ion in the wastewater. Ammonium adsorption by zeolite has been demonstrated to involve ion-exchange process, the rate of which increases with increasing concentration of the ion in solution.^[24,25]

Ammonium adsorption increased with increasing CEC due to removal of amorphous material during the alkali treatment. Similarly, Park and Komarneni^[24] observed NH₄⁺ ion adsorption increased with increasing CEC of the zeolite. However, although the HCl-treated zeolites had lower

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Table 3. CEC and the adsorption of ammonium by the zeolites after treatment with alkali and acid solutions.

Sample no	Treatment	CEC (cmol kg ⁻¹)	Ammonium adsorption (g NH ₄ -N kg ⁻¹)		% CEC occupied by ammonium ions	
			Predelime	Delime	Predelime	Delime
II	Untreated	87.8	1.63	5.56	10.31	35.18
II	NaOH	159.2	1.95	5.68	6.80	19.82
II	NaHCO ₃	161.2	2.12	6.28	7.30	21.64
II	HCl	119.6	3.52	10.42	16.35	48.40
III	Untreated	113.5	2.18	6.08	10.67	29.76
III	NaOH	197.6	2.56	6.52	7.20	18.33
III	NaHCO ₃	181.5	2.75	6.88	8.41	21.05
III	HCl	152.4	4.12	12.44	15.02	45.35
IV	Untreated	106.2	2.29	6.69	11.98	35.00
IV	NaOH	168.9	2.19	6.45	7.20	21.22
IV	NaHCO ₃	153.6	2.47	7.24	8.93	26.19
IV	HCl	138.5	4.98	13.05	19.98	52.35

CEC than the alkali-treated samples, the former samples actually adsorbed higher amount of NH₄⁺ ions than the untreated and the alkali-treated samples (Table 3). This indicates that NH₄⁺ ion adsorption is not only affected by the CEC, which gives the potential maximum adsorption, but also by the dominant cation species on the zeolite. Accordingly, the measured NH₄⁺ ion adsorption values were less than the potential maximum amount (12.2–27.7 g kg⁻¹) calculated from the CEC of the zeolites.

A number of studies have demonstrated the strong affinity of zeolite for cation adsorption corresponding mainly to its high CEC.^[12,18] The cation adsorption capacity varied with the crystalline nature and particle size of zeolite and the ionic composition of the aqueous medium. For example, Nguyen and Tanner^[18] obtained maximum NH₄⁺ ion adsorption values of 5.77 and 8.28 g kg⁻¹ for clinoptilolite and mordenite, respectively. Similarly, Bernal and Lopezreal^[12] obtained a range in NH₄⁺ ion adsorption (8.149 to 15.169 g N kg⁻¹) for a number of zeolites that varied in particle size.

The data on NH₄⁺ ion adsorption show that 6.8 to 52% of CEC of the zeolites was occupied by the NH₄⁺ ions. The wastewater also contained significant quantities of Na⁺ and Ca²⁺ ions (Table 1), which occupied the majority of the zeolite cation exchange sites, thereby strongly competing for adsorption sites. Booker et al.^[26] observed that the amount of NH₄⁺ ion adsorption (4.5 g kg⁻¹) by an Australian zeolite from sewage water was less

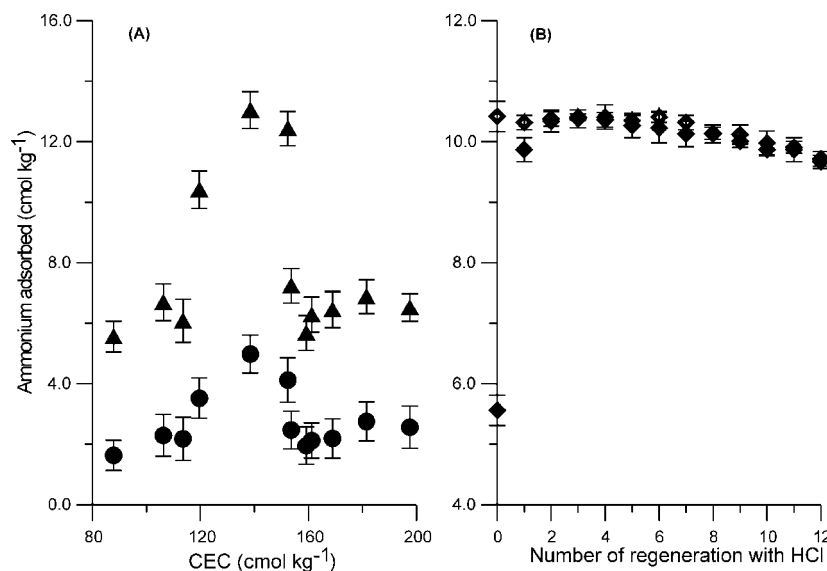


Figure 1. (A) Relationship between CEC and ammonium ion adsorption by the zeolite from the predelime (●) and delime (▲) wastewater; (B) Effect of regeneration of cation exchange sites with 0.5 M HCl leaching on ammonium ion adsorption by the untreated zeolite (◆) and the preacid-treated zeolite (◇) to remove the amorphous material.

than its CEC value, which they attributed to the competition for adsorption sites by other ions. Similarly, Green et al.^[27] observed that the presence of competing cations in secondary sewage reduced NH_4^+ ion adsorption of zeolite by as much as 75%. Whereas, Weber et al.^[25] observed that even in the absence of competing ions, the adsorption maximum reached $23.1 \text{ cmol NH}_4^+ \text{ kg}^{-1}$ for a sample of clinoptilolite, which was only 16.5% of its CEC (140 cmol kg^{-1}). In contrast, Park and Komarneni^[24] observed high levels of incipient NH_4^+ ion adsorption ($26\text{--}46 \text{ g N kg}^{-1}$) for four zeolite species when they were treated with saturated NH_4Cl solution. The amount of NH_4^+ ion adsorbed exceeded the CEC ($177\text{--}267 \text{ cmol kg}^{-1}$) of the zeolites, apparently caused by salt occlusion.

From the volumes of wastewater streams and their NH_4^+ ion concentrations, the total amount of NH_4^+ ion generated by the fellmongery plant was calculated (Table 4). The quantity of zeolite required to adsorb all the NH_4^+ ions from the wastewater was then estimated, based either on NH_4^+ ion loading measured in the present study, or the maximum potential loading

Removal of Ammonium Ions by Zeolite**1869****Table 4.** Concentration of ammonium ion in the wastewater samples and the quantities of HCl-treated zeolite required to retain the ammonium ions.

Wastewater sample	Volume (m ³ day ⁻¹)	Ammonium concentration (g NH ₄ -N m ⁻³)	Amount of ammonium (kg day ⁻¹)	Zeolite required to remove ammonium (kg day ⁻¹)	
				Measured*	Potential**
Predelime	12	715	8.58	2430	510
Delime	36	1210	43.56	4180	2600

*Based on the measured maximum ammonium adsorption = 3.52 and 10.42 g NH₄-N kg⁻¹ for predelime and delime wastewater, respectively; **Based on the potential maximum ammonium adsorption = 16.74 g NH₄-N kg⁻¹ zeolite

calculated from the CEC value (Table 4). It was estimated that approximately 6,610 kg of zeolite would be required daily to remove NH₄⁺ ions from these two wastewater streams.

Regeneration of CEC

As expected, the adsorption of NH₄⁺ ions by the untreated zeolites increased with 0.5 M HCl leaching to regenerate the cation exchange sites and the adsorption approached that of the samples originally treated to increase the CEC (Fig. 1B). The results also indicate that even after 12 cycles of regeneration of cation exchange sites, NH₄⁺ ion adsorption by the zeolites was not greatly reduced. Leaching with 0.5 M HCl released both the NH₄⁺ ions and other cations (Ca²⁺, Mg²⁺, K⁺, and Na⁺) from the exchange sites of the zeolites. Although during 0.5 M HCl leaching most of the exchange sites on the zeolites were made available for NH₄⁺ ion adsorption from the wastewater, other cations present in the wastewater competed for adsorption sites and NH₄⁺ ion adsorption never reached the potential maximum calculated from CEC.

CONCLUSIONS

A number of zeolites obtained from the New Zealand Resource Refineries Ltd. possessed significant amounts of CEC (> 100 cmol kg⁻¹) and can be used to remove cations from waste streams. Removal of amorphous materials from the zeolites using alkali solutions resulted in significant increases in

the CEC of the zeolites. The CEC of the zeolites indicated that these samples can hold a potential maximum of between 12.2 to 27.7 g $\text{NH}_4\text{-N kg}^{-1}$ zeolite.

The NH_4^+ ion adsorption values obtained in the column experiment were less than the potential maximum amount calculated from the CEC of the zeolites, apparently due to the presence of competing cations. Ammonium ions in the wastewater occupied between 6.8 to 52% of the cation exchange sites in the zeolites, the majority being occupied by Na^+ and Ca^{2+} . Initial estimates indicated that daily approximately 6,610 kg zeolite would be required to remove all the NH_4^+ ions from the wastewater. The NH_4^+ ion adsorption capacity of the zeolites was regenerated by leaching the NH_4^+ ion-enriched samples with 0.5 M HCl. Even after 12 regeneration cycles with 0.5 M HCl, the NH_4^+ ion adsorption capacity of the zeolites was not compromised, indicating long-term efficacy of the regenerated zeolites which translates to reduced cost in wastewater treatment.

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