



# Ammonia removal from wastewater by ion exchange in the presence of organic contaminants

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## Abstract

The scope of this study was the removal of ammonium by ion exchange from simulated wastewater. The study looks at the effect of organics upon ammonium ion exchange equilibrium uptake. The ion exchangers included a natural zeolite clinoptilolite, and two polymeric exchangers, Dowex 50w-x8, and Purolite MN500. The organic compounds studied included citric acid and a number of proteins. The traditional method for removal of ammonium and organic pollutants from wastewater is biological treatment, but ion exchange offers a number of advantages including the ability to handle shock loadings and the ability to operate over a wider range of temperatures. The results show that in most of the cases studied, the presence of organic compounds enhances the uptake of ammonium ion onto the ion exchangers.

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## 1. Introduction

The traditional method for ammonium and organic removal from municipal and industrial wastewaters is based on biological treatments [1]. As discharge limits of various pollutants becomes more stringent, ion exchange and adsorption become more interesting as possible treatment methods.

In water treatment systems where the ammonium ion is being removed it is possible that organic pollutants are also present. Heterotrophic bacteria, which consume the organic species, inhibit the growth and activity of nitrifying bacteria to consume ammonia. In this situation ion exchange offers an alternative method in the removal of the ammonium ion.

Ammonium removal by ion exchange is also used in the aquaculture industry where water is recirculated [2].

Complete removal of ammonia is required due to its extreme toxicity to most fish species. Aquaculture occasionally requires water to be cool ( $\sim 10^{\circ}\text{C}$ ), which is an unsatisfactory temperature for many biological methods. Biological methods (nitrification) do not respond well to shock loads of ammonia, and unacceptable peaks in effluent ammonium concentration may result in such cases. Fluctuating concentrations of ammonium are more toxic to fish than moderate yet constant concentrations.

One ion exchanger with a high affinity for ammonium ion is clinoptilolite, a naturally occurring zeolite [3–6]. Earlier studies have shown that clinoptilolite, and certain other natural zeolites can be effective in removing ammonia from wastewater [7]. More recently, the availability of polymeric macronet exchangers (Purolite) has led to more applications of ion exchange in environments that are unsuitable for other exchangers [8].

Clinoptilolite is reported to have a classical aluminosilicate cage like structure and therefore exhibits significant macroporosity [9]. Likewise macronet resins are reported to have significant macroporosity. In both

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cases this may be a factor in determining their ion-exchange behaviour in the presence of high molecular weight contaminants such as proteins.

One of the significant issues in the application of laboratory studies to industrial wastewater treatment is the effect which contaminants in actual wastewater have upon the technique used. In this study we chose contaminants which were representative of two groups commonly found in wastewater, namely organic acids, and proteins. The ammonium concentrations of interest may also be quite specific to the source of the wastewater. For example, aquaculture water requires ammonia removal at levels of less than 1 mg/l, whereas in municipal wastewater treatment levels may be up to ten times this level, and in industrial wastewater levels may exceed 100 mg/l. Therefore, a significant range of ammonium ion concentrations was included in the study.

## 2. Experimental

The experimental goal was to determine the equilibrium distribution of ammonium ion between the solid and aqueous phases. All experiments were carried out by contacting the solution with the solid phase in a single batchwise step.

Batch equilibrations of three different cationic ion exchangers (Clinoptilolite, Dowex 50w-x8, and Purolite MN500) in the sodium form, with solutions of ammonium ion (chloride as the co-ion), were conducted. Each exchanger was preconditioned into the sodium form by contacting the solid with aqueous sodium chloride solution (10 g/l) in a series of batchwise steps, then washed with distilled water.

In selected experiments individual organics were added to determine the effect of the presence of organic compounds upon sodium/ammonium ion equilibrium. Fixed volumes (80 ml) of ammonium chloride solution having concentrations in the range 71.14–593.1 mg/l (25–200 mg/l of  $\text{NH}_4^+$ ) were contacted with 0.8 g of dry exchanger solid. A series of preliminary trials showed that steady-state equilibrium was achieved within 4 days. Each sample was allowed to equilibrate for 6 days, with periodic agitation, prior to analysis for the final ammonium ion concentration. The final concentration of organic species was not measured since they were added only to determine the effect of their presence on the sodium/ammonium ion exchange equilibrium.

Following equilibration, solid and liquid phases were separated and the final ammonium concentrations determined using a Hach (50250) ammonia ion selective electrode. The sample preparation procedure required the addition of alkaline buffer to ensure that the ammonia was essentially un-ionised prior to analysis. The ammonia analyses were crosschecked using the Nesslerisation technique on several samples [10].

## 3. Results and discussion

Fig. 1 shows the results of the equilibration of ammonium ion onto clinoptilolite in the presence of sodium ion (no organics present). The data are presented as solid phase ammonium ion concentration (mg of  $\text{NH}_4^+$  per gram of resin) plotted against liquid phase ammonium ion concentration. The Langmuir model provided a close fit for the ion-exchange equilibrium. The Langmuir model assumes only one solute molecule per site, and also assumes a fixed number of sites. Whilst the model was developed for adsorption it is clear that the assumptions and the experimental data work well for ion exchange in this case. In contrast, the Freundlich model provided a poor fit for the experimental data.

In a previous study [11] the effects of the presence of a range of organic compounds on the ion-exchange equilibrium uptake of ammonium ion were determined. In each case the presence of organic compounds enhanced the uptake of ammonium ion onto clinoptilolite. Fig. 2 shows that the presence of lipase in a

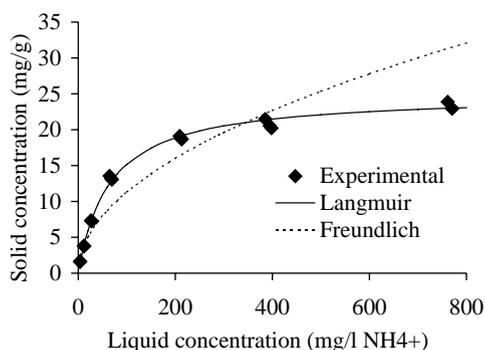


Fig. 1. Ammonium ion uptake equilibria onto clinoptilolite.

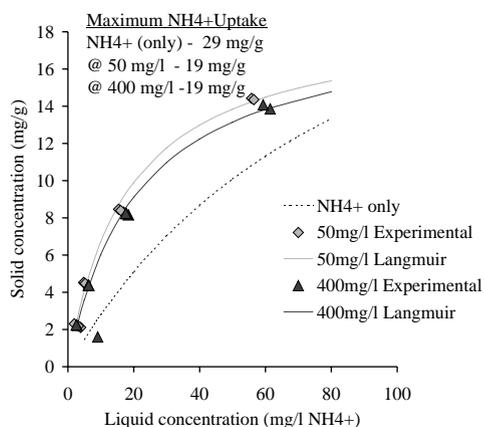


Fig. 2. Ammonium ion uptake equilibria onto clinoptilolite in the presence of lipase from *Candida rugosa*.

lactose-based formulation significantly enhanced the equilibrium uptake of ammonium ion. In these experiments lipase from the yeast *Candida rugosa* was added as a mixture comprising 70 wt% lactose, 30 wt% lipase. The 50 and 400 mg/l concentrations shown in the legend of Figs. 2–11 refer to the organic concentration.

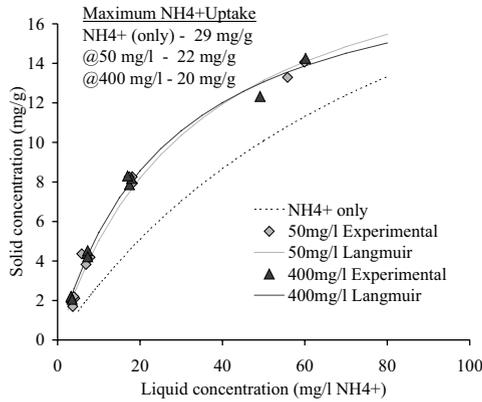


Fig. 3. Ammonium ion uptake equilibria onto clinoptilolite in

Fig. 3 shows that there is also enhancement of ammonium ion uptake onto clinoptilolite in the presence of whey protein, showing behaviour similar to that observed in the presence of lipase.

In the case of clinoptilolite, ammonia uptake was also determined at much higher concentrations (> 100 mg/l)

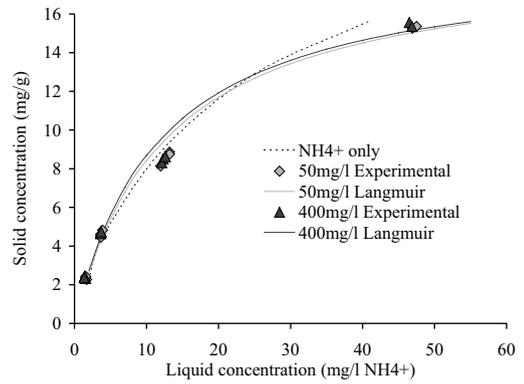


Fig. 6. Ammonium ion uptake equilibria onto Dowex 50w-x8 in the presence of whey protein.

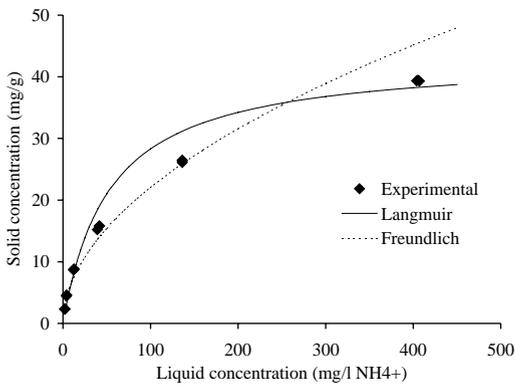


Fig. 4. Ammonium ion uptake equilibria onto Dowex 50w-x8.

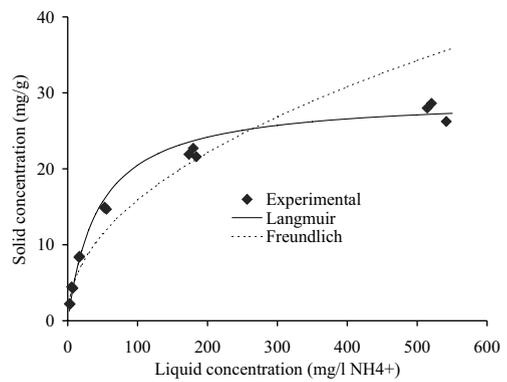


Fig. 7. Ammonium ion uptake equilibria onto Purolite MN500.

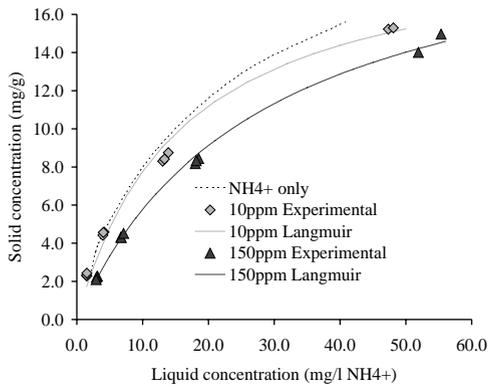


Fig. 5. Ammonium ion uptake equilibria onto Dowex 50w-x8 in the presence of citric acid.

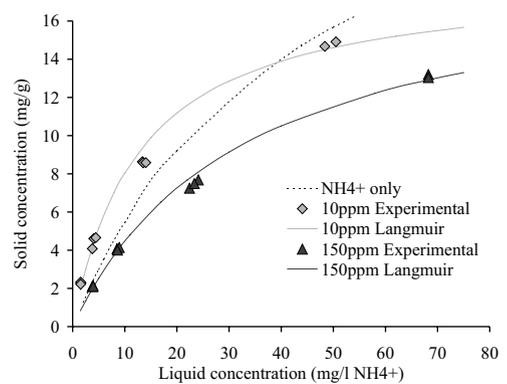


Fig. 8. Ammonium ion uptake equilibria onto Purolite MN500 in the presence of citric acid.

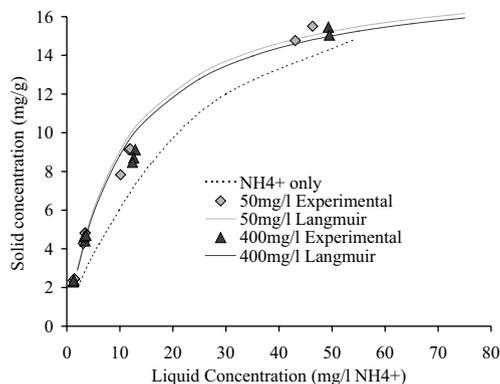


Fig. 9. Ammonium ion uptake equilibria onto Purolite MN500 in the presence of whey protein.

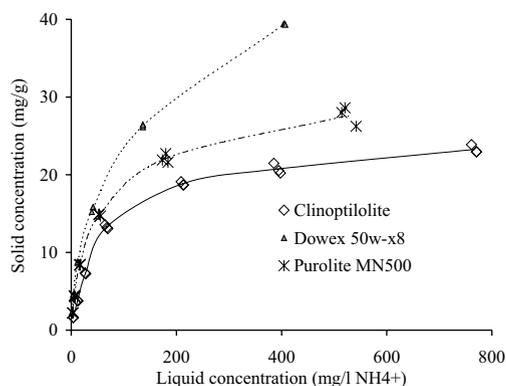


Fig. 10. Ammonium ion uptake equilibria onto Clinoptilolite, Dowex 50w-x8, and MN500.

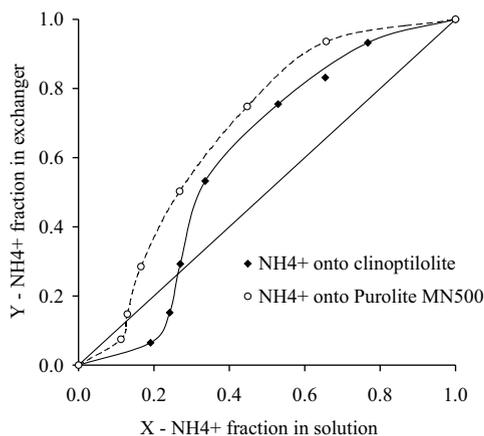


Fig. 11. Ammonium ion exchange equilibria of Clinoptilolite and Purolite MN500.

and a total limiting capacity for ammonium ion determined. These values are shown in Figs. 2 and 3 for clinoptilolite. In both cases it was established that in

the presence of lipase and in the presence of whey protein, total uptake of ammonia at the maximum limit becomes less when compared with uptake in the absence of these contaminants. Therefore, the “enhancements” in ammonia uptake are only observed within a limited range of solution phase concentrations.

Fig. 4 shows the equilibrium uptake of ammonium ion onto Dowex 50w-x8 in the presence of sodium ion. In this case neither the Langmuir nor the Freundlich isotherm models provide an entirely accurate fit for the experimental data. It is possible that changes in the external solution ionic concentration affect exchanger structure. Product information for Dowex 50w-x8 indicates shrinkage or swelling in the range 0–8% depending on the ionic radius of the cation present [12]. The presence of ammonium ions may modify slightly the internal structure of the resin, changing the microporosity and thus access to the fixed sites. Such changes can depend upon hydrated ionic radii of both counter-ions present within the exchanger. Ionic radius data for sodium ion and ammonium ion are shown in Table 1 [13].

Shrinking and swelling also depend to some extent on the degree of cross-linking in polymeric resins. In clinoptilolite the zeolite structure changes insignificantly with different cations of different size and this may offer some explanation why the Langmuir isotherm fitted the uptake data for clinoptilolite reasonably well, whereas the fit in the case of Dowex 50w-x8 was poor.

In our earlier study [11] it was found that ammonium ion uptake was enhanced in the presence of citric acid even though some competition for sites by hydrogen ions might be expected. Fig. 5 shows data for the equilibrium uptake of ammonium ion onto Dowex 50w-x8 resin in the presence of citric acid. Only a slight decrease in uptake of ammonium ion is observed as the citric acid concentration increases.

One possible explanation for the observed enhancement in uptake is that the presence of the organic may reduce the surface tension of the aqueous phase to the point of enhancing access of the aqueous phase to the macropores of the exchanger. The presence of citric acid reduces the surface tension of water [14]. Clinoptilolite and Purolite MN500 both contain micropores and macropores and were the two exchangers to show enhancement in the presence of an organic. Dowex 50w-x8, which does not contain macropores, did not

Table 1  
Ionic radii

	Ionic radius (Å)	Hydrated radius (Å)
$\text{NH}_4^+$	1.43	5.35
$\text{Na}^+$	0.95	7.9

show any  $\text{NH}_4^+$  enhancement in the presence of any organic. However further detailed experimentation would be required to determine any definitive link between surface tension and changes in ion exchange uptake.

Fig. 3 showed that the presence of whey protein enhanced the uptake of  $\text{NH}_4^+$  onto clinoptilolite. In contrast, Fig. 6 shows that in the presence of whey protein there is no enhancement of uptake onto Dowex 50w-x8 at low concentrations of ammonium ion. At higher concentrations of ammonium ion the relative uptake is reduced.

Fig. 7 shows that the Langmuir model gave a reasonable fit for ammonium ion uptake onto Purolite MN500, although the fit is not as good as that for clinoptilolite. The observations are similar to those for Dowex 50w-x8 (see Fig. 6). Although there is a good fit to the Langmuir isotherm it is likely that Purolite MN500 cannot swell significantly since the resin is hyper-crosslinked.

Fig. 8 shows that ammonium ion uptake onto Purolite MN500 is enhanced in the presence of citric acid. However, at the higher hydrogen ion concentration the competition for sites from hydrogen ions may become significant resulting in a reduction in the overall enhancement.

Data shown in Fig. 9 show that enhanced ammonium ion uptake onto MN500 was observed across a range of concentrations of whey protein. The enhancement is not as large as was observed in the case of clinoptilolite (see Fig. 3). The high overall exchange capacity of Purolite MN500 relative to clinoptilolite may explain this difference.

Fig. 10 shows that of the three ion-exchangers studied here, Dowex 50w-x8 has the highest capacity for ammonium ion. Purolite MN500 shows the next to highest capacity. The lowest capacity is exhibited by clinoptilolite. From the Langmuir isotherms for ammonium uptake alone, shown in Figs. 1 and 7, ion fraction values for ammonium ion in each phase were calculated and these are plotted in Fig. 11. These data show that Purolite MN500 has a higher selectivity for ammonium ions relative to sodium ions, in comparison to clinoptilolite. At equal molar concentration ( $X = 0.5$ ) the selectivity is, clinoptilolite = 2.7, Purolite MN500 = 4.3.

In applications of ammonium removal from industrial water, or recirculated waters from aquaculture, other cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) will be present. Even freshwaters contain a low concentration of salinity. These other cations will compete for sites, hence lowering the effective capacity for the ammonium ion. The higher selectivity shown by Purolite MN500 means that a larger percentage of the available sites will be occupied by the ammonium ion. The selectivities of ammonium relative to  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  are not known, however,  $\text{Na}^+$  is the most common cation present in water. However Purolite MN500 is unlikely to

be adequately selective for ammonium ions in marine water.

If a larger percentage of the sites in Purolite MN500 relative to clinoptilolite are occupied by ammonium ions regeneration is also much easier. This is due to the ease of regenerating ion exchange resins under alkaline conditions to convert  $\text{NH}_4^+$  into  $\text{NH}_3$ . Other cations are only removed by equilibrium driving forces, and therefore may be more difficult to achieve.

#### 4. Conclusions

The results show the highest  $\text{NH}_4^+$  uptake was observed in the case of Dowex 50w-x8. Purolite MN500 exhibited lower degrees of ammonium ion uptake. Clinoptilolite showed the lowest uptake of ammonium ion.

Ammonium ion uptake onto Clinoptilolite and onto Purolite MN500 are accurately described by the Langmuir model. Uptake onto Dowex 50w-x8 was described by the Langmuir model with much less accuracy.

The presence of citric acid, and whey protein increased the observed uptake of  $\text{NH}_4^+$  onto clinoptilolite and onto Purolite MN500. No increase was observed for the *net* uptake of  $\text{NH}_4^+$  onto Dowex 50w-x8. In the cases of clinoptilolite and Purolite MN500, the influence of surface tension changes due to the presence of organics upon access of counter-ions to fixed sites in the exchangers could offer a possible explanation, but would require separate experimental measurements specifically focussed on surface tension variations.

In contrast, Dowex 50w-x8, which does not exhibit significant macroporosity, did not show any  $\text{NH}_4^+$  uptake enhancement in the presence of any organic.

It is concluded that determination of the effect of the presence of organics upon the physical properties of each of the exchangers would be valuable for future study as a means of furthering the understanding of observed changes in ion-exchange properties.

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#### References

- [1] Kelly G. Environmental engineering. Maidenhead, England: Mc-Graw Hill Publishing Company, 1996.

- [2] Dryden HT. Ammonium ion removal from dilute solutions and fish culture water by ion exchange. PhD thesis, Heriot-Watt University, Edinburgh, UK, 1984.
- [3] McVeigh RJ. The enhancement of ammonium ion removal onto columns of clinoptilolite in the presence of nitrifying bacteria. Ph.D. thesis, The Queen's University of Belfast, Northern Ireland, United Kingdom, 1999.
- [4] Woods N. The removal of ammonia from industrial wastewater. M.Sc. Research Dissertation, The Queen's University of Belfast, United Kingdom, 1997.
- [5] Semmens MJ, Klieve J, Schnobrich D, Tauxe G. Modelling ammonium exchange and regeneration on clinoptilolite. *Water Res* 1981;15:655–66.
- [6] Ames LL. Zeolite removal of ammonium ions from agricultural wastewaters. Proceedings of the 13th Pacific Northwest Industrial Waste Conference, Washington State University, Pullman, Washington, 1967. p. 135.
- [7] Nguyen ML, Tanner CC. Ammonia removal from wastewaters using natural New Zealand zeolites. *N Z J Agric Res*, 1998;41:427–46.
- [8] Dale JA, Nikitin NV, Moore R, Opperman D, Crooks O, Naden D, Belsten E, Jenkins P. Macronet, the birth and development of a technology. In: Gregg JA, editor, Ion exchange at the millennium. London: Imperial College Press, 2000. p. 261–8.
- [9] Tsitsishvili GV, Andronikashvili TG, Kirov GN, Filixova LD. Natural zeolites, 1st ed.. London: Ellis Horwood, 1992.
- [10] Eaton AD, Cleceri LS, Greenberg AE, editors. Standard methods for the examination of water and wastewater, 19th ed. Washington DC, USA: American Public Health Association, 1995.
- [11] Jorgensen TC, Weatherley LR. Ion exchange removal of ammonium ion from wastewater onto clinoptilolite in the presence of organics. Sixth World Congress of Chemical Engineering, Melbourne, Australia, 2001.
- [12] Dow Chemical (2002) (<http://www.serva.de/products/knowledge/071119.shtml>) and (<http://www.dow.com/>).
- [13] Robinson RA, Stokes RH. Electrolyte solutions. UK: Butterworth Publications, Pitman, 1959.
- [14] Timmermans J. The physico-chemical constants of binary systems in concentrated solutions. London: Interscience Publishers, 1960.