University of Durham
Department of Earth Sciences

An Investigation into the Adsorption of Metals and Ammonia onto Natural Zeolite Samples Supplied by Euremica Environmental Ltd

5th November 2003

Dr Christopher Johnson
Derek Johnson

Contact:
waste.management@durham.ac.uk
(0191) 3342321

1. Introduction

This report outlines work carried out between July and October 2003 investigating the adsorption of cations onto natural zeolite materials supplied by Euremica Environmental Ltd.

2. Samples

The work carried out for this report was conducted with two batches of fine material and a further batch of coarser grading supplied by Euremica Environmental Ltd. The first batch of fine material was delivered in mid July, the second batch arriving in two stages, on 20/08/03 and 01/09/03, were reported to be identical material Both fine materials were received milled with the initial material stated to be <50μm and >30μm. For the adsorption isotherms sub-samples were taken from these materials using a spatula, the fine grain size and apparent homogenous nature of the material indicating that the assumption that 1g samples would be representative was valid. The coarser material (<0.9mm) was also supplied in mid July and was used for trial runs of the zeolite as an ion exchange column.

3. Adsorption Isotherms

The ability of the supplied zeolite to adsorb either one of seven metal cations or ammonium was assessed by measuring adsorption isotherms for solutions of the cations (as either chlorides or nitrates). The cation species investigated and the salts used to produce the starting solutions are set out in table 1. Where possible chlorides were used, however the chlorides of lead and chromium are poorly soluble when compared with the others and the corresponding nitrates were used as an alternative.

Table 1. Cations used for adsorption studies and the salts from which they were prepared.

Cation	Stock solution prepared from
NH_4^+	NH_4Cl
Cu^{2+}	$Cu(II)Cl_2 \cdot 2H_2O$
Zn^{2+}	$ZnCl_2$
Pb^{2+}	$Pb(II)NO_3$
Ni^{2+}	$Ni(II)Cl_2 \cdot 6H_2O$
Co^{2+}	$Co(II)Cl_2 \cdot 6H_2O$
Cr^{3+}	$Cr(III)NO_3 \cdot 9H_2O$
Cd^{2+}	$CdCl_2 \cdot 2.5H_2O$
Na^+	$NaCl$

3.1 Methodology

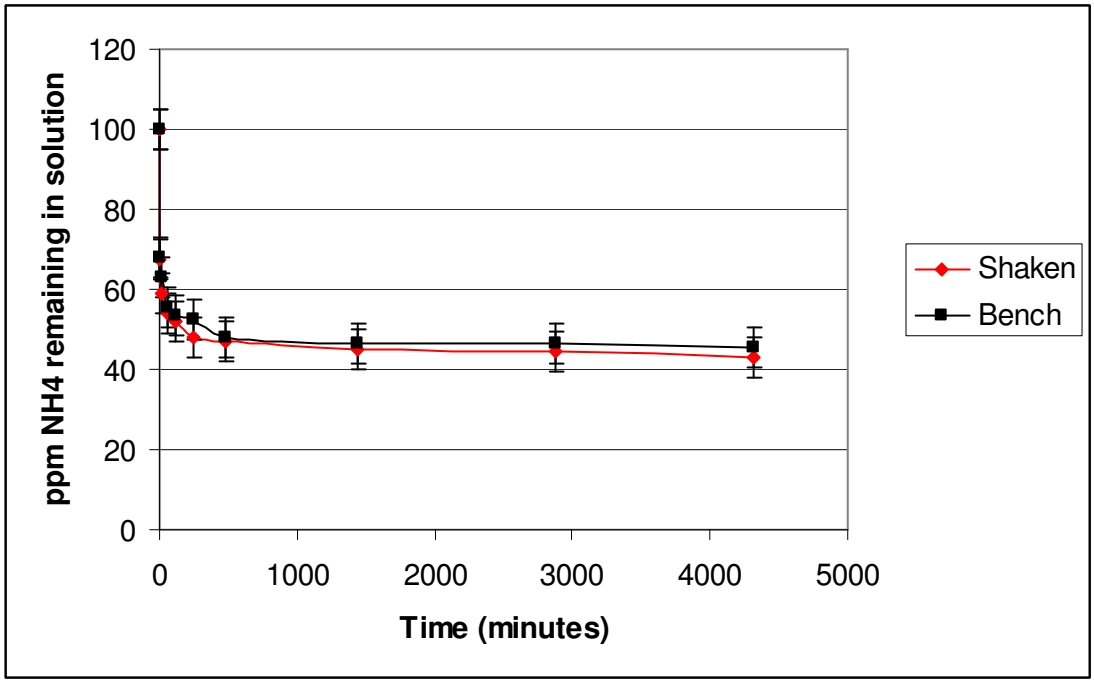
Adsorption isotherms were measured by adding 100ml of cation solutions of increasing concentration to 1g samples of zeolite in sealed bottles. The bottles were left to equilibrate for 24 hours with periodic manual agitation. At the end of the 24 hours equilibration period the resulting solutions were filtered (using 45μm cellulose nitrate filters). Filters were pre washed with distilled water and the first 5-10ml of each filtered solution was discarded. The solutions were then analysed to determine

the concentration of the original cations remaining in solution. The solid phase concentration of each cation was then calculated by difference and plotted against that of the liquid to construct the isotherm. The resulting data was analysed to determine, as far as possible with the limited data set, whether the behaviour fitted with that of any of the well known adsorption isotherm models.

3.1.1 Time to equilibrium

In order to prove that the 24 hour contact period between the zeolite and solution was sufficient, and also that the mixtures received sufficient agitation, a separate trial was performed using a 100mg/l ammonium solution. The solution was mixed with the zeolite (One litre solution to 10grams of solid) and left to equilibrate. Sub-samples of 10ml were removed after different periods of time and filtered prior to analysis. The change in concentration of both solutions over a 72 hour period was monitored and the results are presented in figure 1. No correction was made for the reduction in liquid volume as subsequent samples were removed.

Figure 1. Concentration of ammonium remaining in solution (initially 100mg/l) against time of contact with zeolite.



3.1.2 Adsorption trials

Adsorption isotherms were constructed for the zeolite samples with the eight cations. For the trials using the initial batch of zeolite, equal concentrations (by mass of cation) were used in order to provide results with which to target further points upon the adsorption isotherm. After reporting these initial results, it was requested by Euremica that the further points were performed using the second batch of zeolite. Therefore further points were not then measured for the first batch of material. The starting concentrations chosen for the second batch of zeolite were based upon the results of the first batch and consideration of the relative atomic mass of the different species. The consequences of measuring isotherms for two different materials is that less points are available for the definition of both isotherms and that the definitions of

the isotherms for the first batch are limited by having been performed as a guide for future work, which was not then carried out.

The initial concentrations of the solutions used to construct the adsorption isotherms are given in table 2 All concentrations are in milligrams per litre (mg/l) of the cation.

Table 2. Concentrations of the solutions prepared prior to contact with zeolite samples.

Cation	Starting strengths of Solutions (mg/l cation)	
	Batch 1	Batch 2 *
NH_4^+	10,30,60,100,200	10,30,60,**100**,200
Cu^{2+}	10,30,60,100,200	50,**100**,200,300,400
Zn^{2+}	10,30,60,100,200	25,50,**100**,200,300
Pb^{2+}	10,30,60,100,200	125,250,**500**,1000,2000
Ni^{2+}	10,30,60,100,200	25,**50**,100,200,300
Co^{2+}	10,30,60,100,200	10,25,**50**,100,200
Cr^{3+}	10,30,60,100,200	25,50,**100**,200,300
Cd^{2+}	10,30,60,100,200	25,50,**100**,200,300
Na^+	Not Applicable	200 in reverse step

(* Samples highlighted in bold were used for the reverse isotherm points using Na – 10 ml of Na solution was add at 2000mg/l to 90ml of the solution remaining after the forward isotherm)

3.1.3 De-sorption trials

Spot tests to investigate the desorption of the exchanged cations in response to an excess of a competing species were performed for the second series of isotherms. These tests were performed by carefully removing 10ml of the equilibrated solution for analysis and replacing it with an equal volume of 2000ppm Na^+ solution. The resulting solution initially containing 200ppm Na was then allowed to re-equilibrate with the zeolite and the final concentration of the cation of interest determined. From this the amount of metal released from the zeolite was computed and the results compared with the forward isotherm.

3.1.4 Analytical Methods

The analysis of the final solution concentrations were performed by Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) using a Perkin Elmer Optima 3100RL. Synthetic standards were used for calibration with an yttrium internal standard. Analysis of ammonium was carried out using a Camspec M202 UV-vis spectrophotometer measuring adsorption at 630nm for samples mixed with excess hypochlorite, phenol and sodium nitroprusside, in an alkaline solution, the ammonium being transformed to indophenol producing a blue colouration. Ammonium analytical standards were diluted from the stock solution prepared for the adsorption isotherms.

3.2 Results

The adsorption isotherms for the eight cations with the two different zeolite samples are shown in figures 2-9. Also shown in these figures are the curves formed by fitting either the Langmuir or Freundlich isotherm models to the data produced.

Figure 2a Ammonium adsorption with initial batch of zeolite

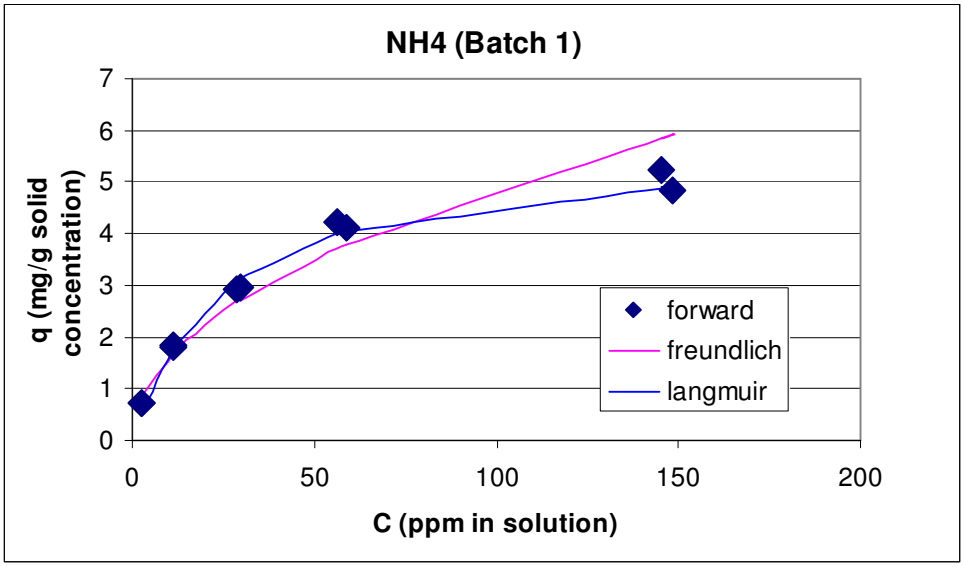


Figure 2b Ammonium adsorption with second batch of zeolite

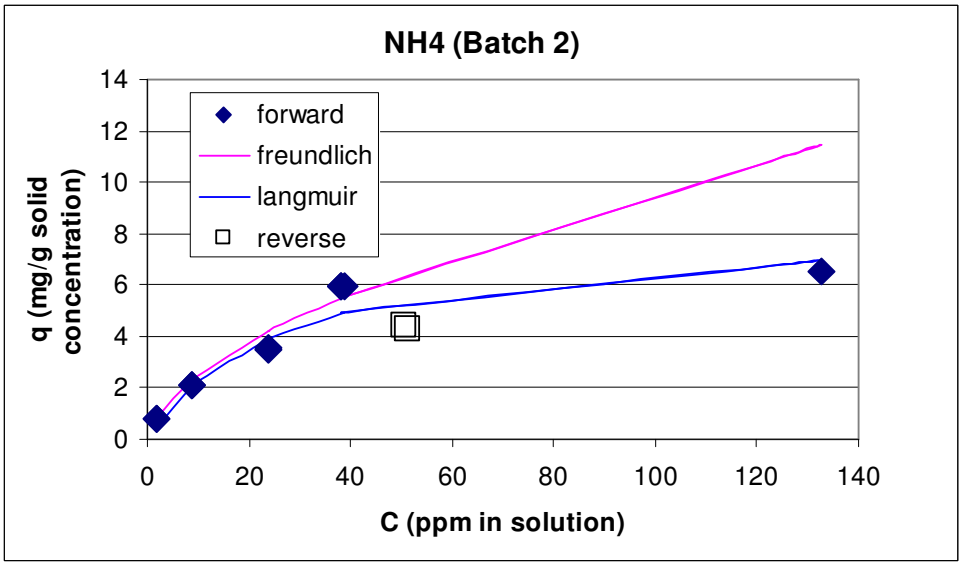


Figure 3a Copper adsorption with initial batch of zeolite

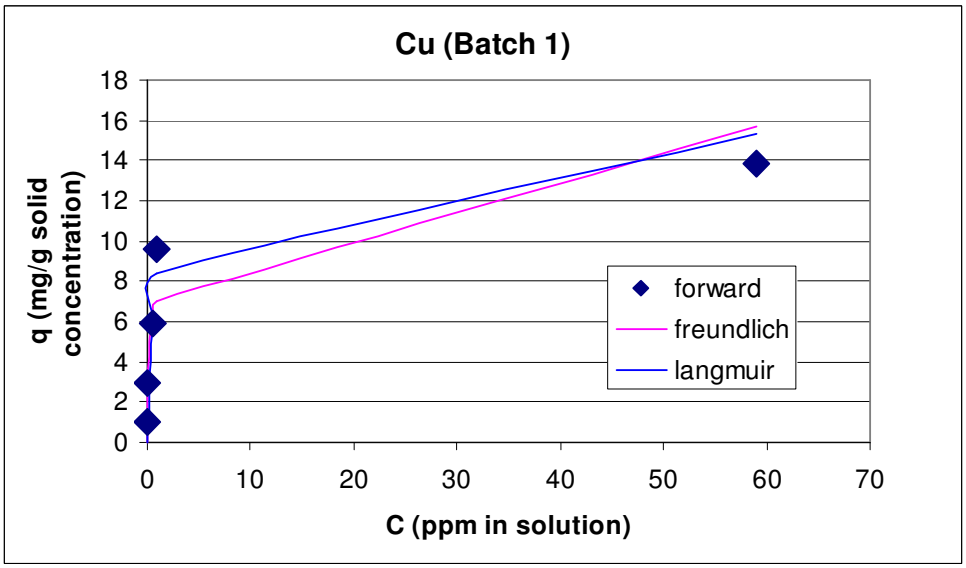


Figure 3b Copper adsorption with second batch of zeolite

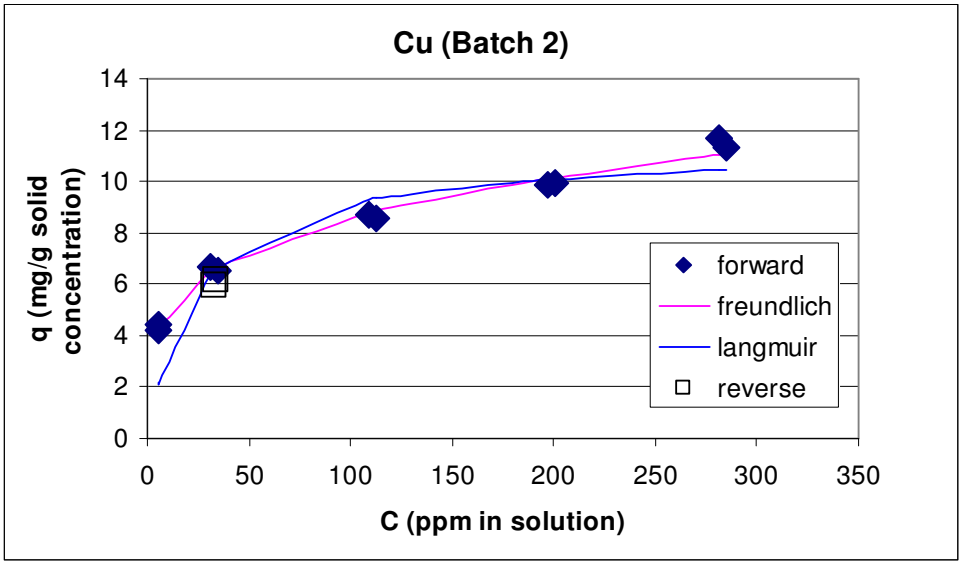


Figure 4a Zinc adsorption with initial batch of zeolite

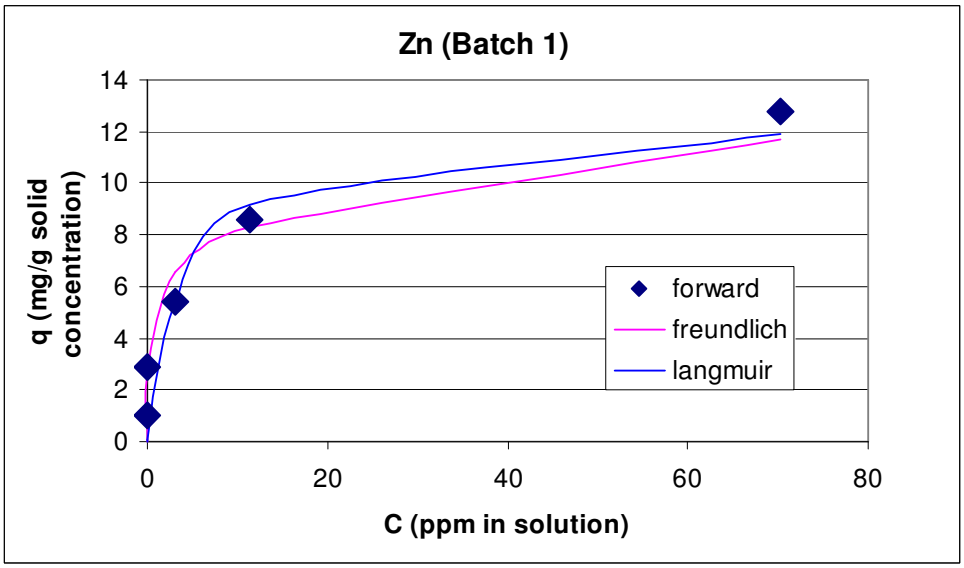


Figure 4b Zinc adsorption with second batch of zeolite

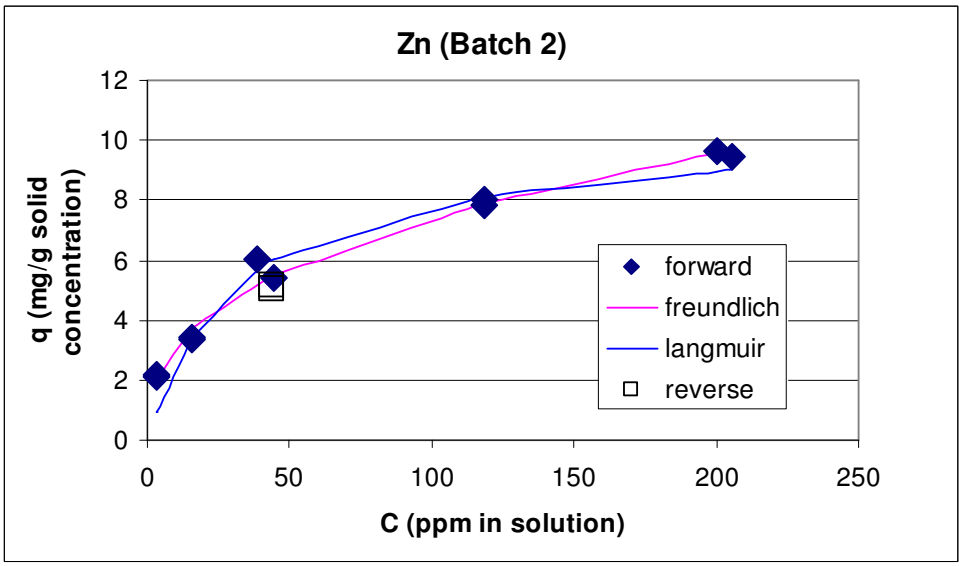


Figure 5a Lead adsorption with initial batch of zeolite

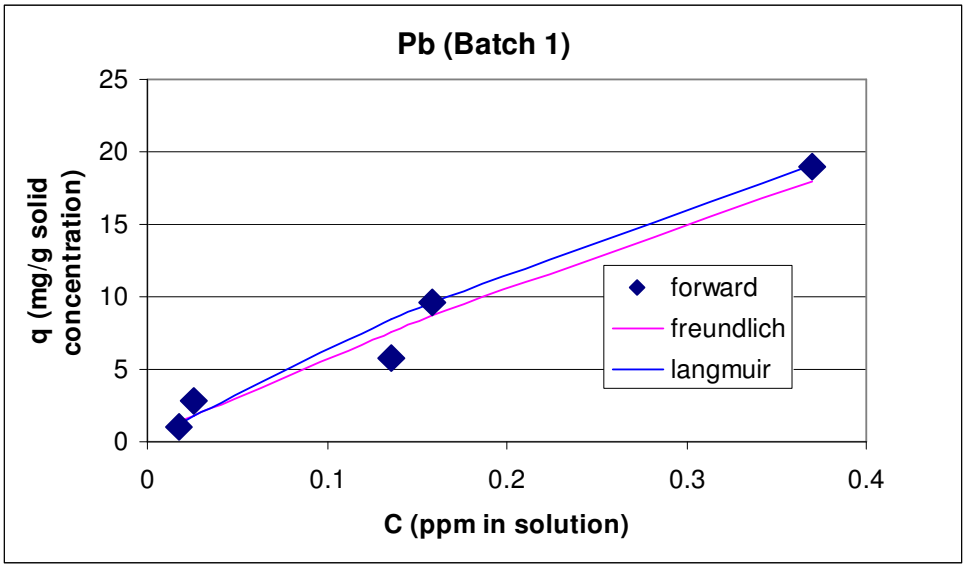


Figure 5b Lead adsorption with second batch of zeolite

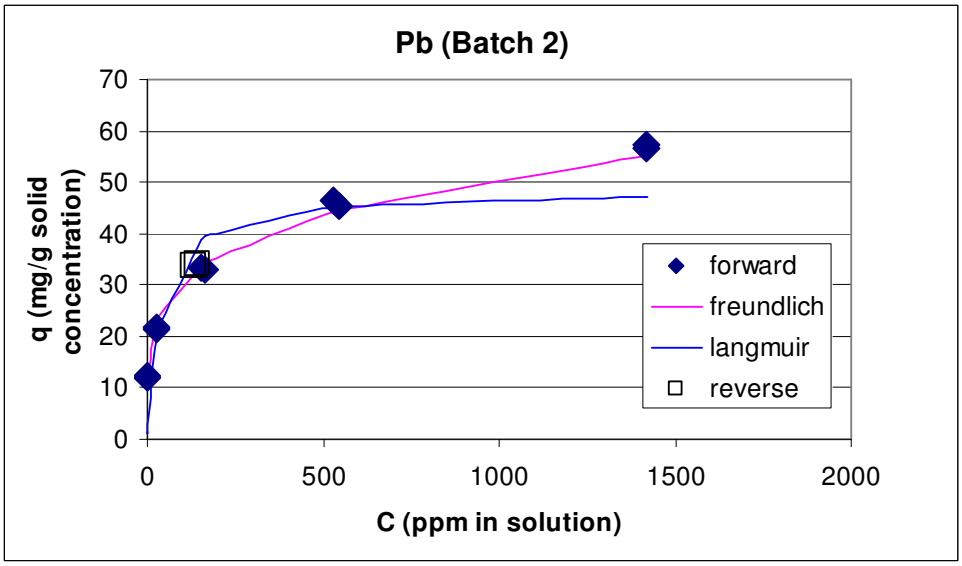


Figure 6a Nickel adsorption with initial batch of zeolite

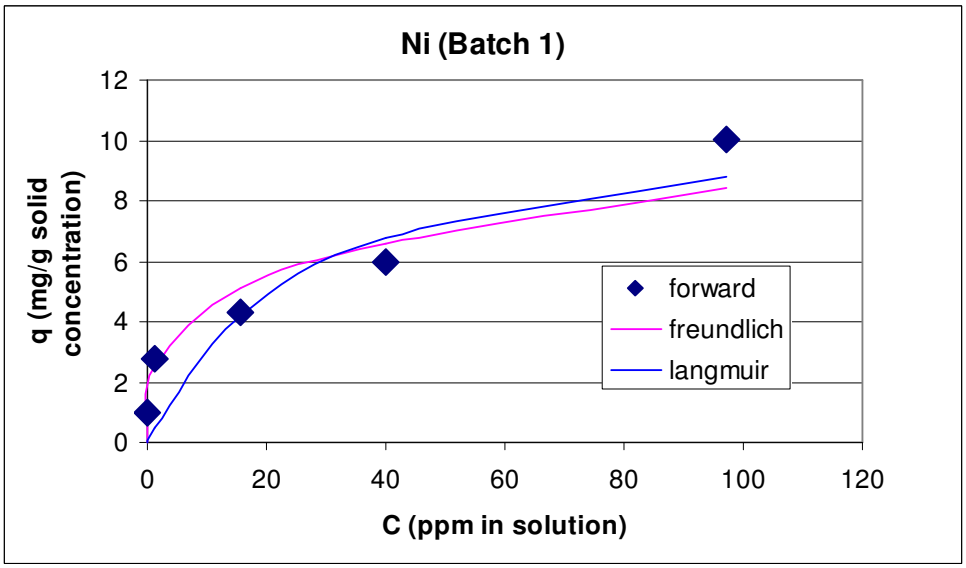


Figure 6b Nickel adsorption with second batch of zeolite

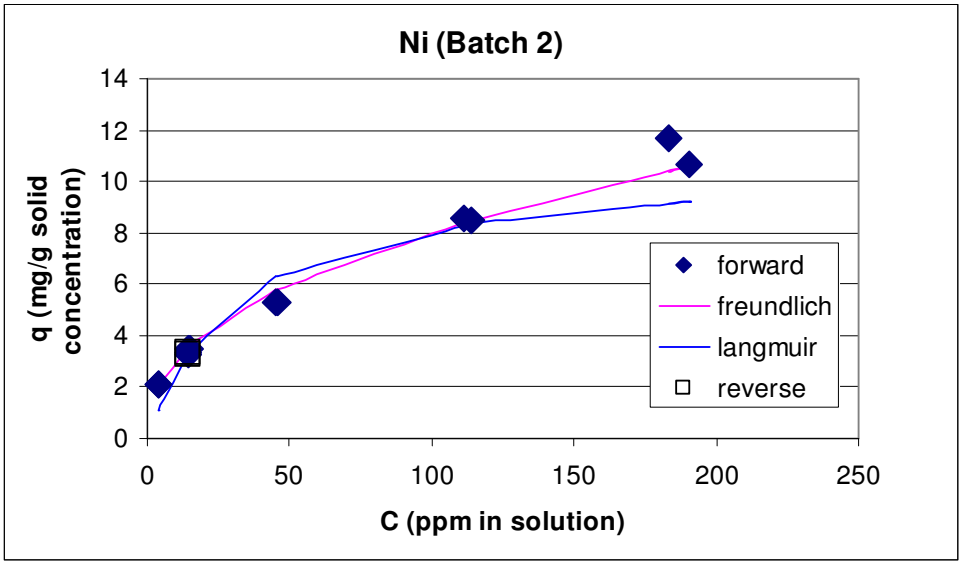


Figure 7a Cobalt adsorption with initial batch of zeolite

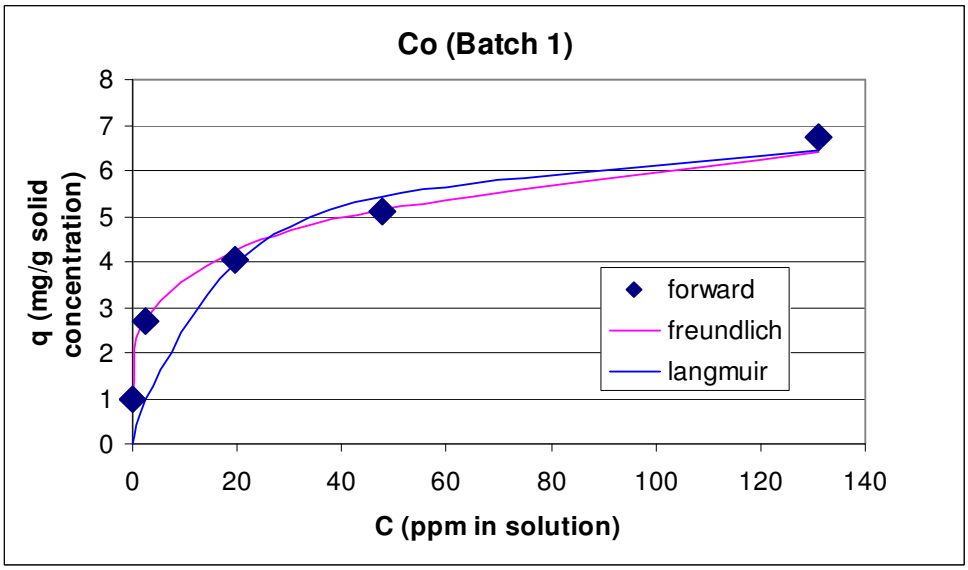


Figure 7b Cobalt adsorption with second batch of zeolite

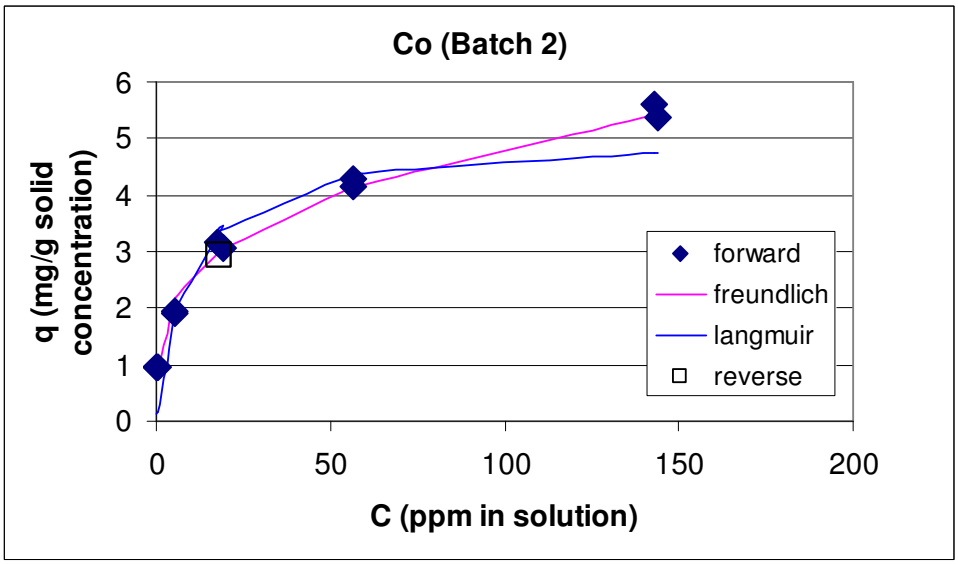


Figure 8a Chromium adsorption with initial batch of zeolite

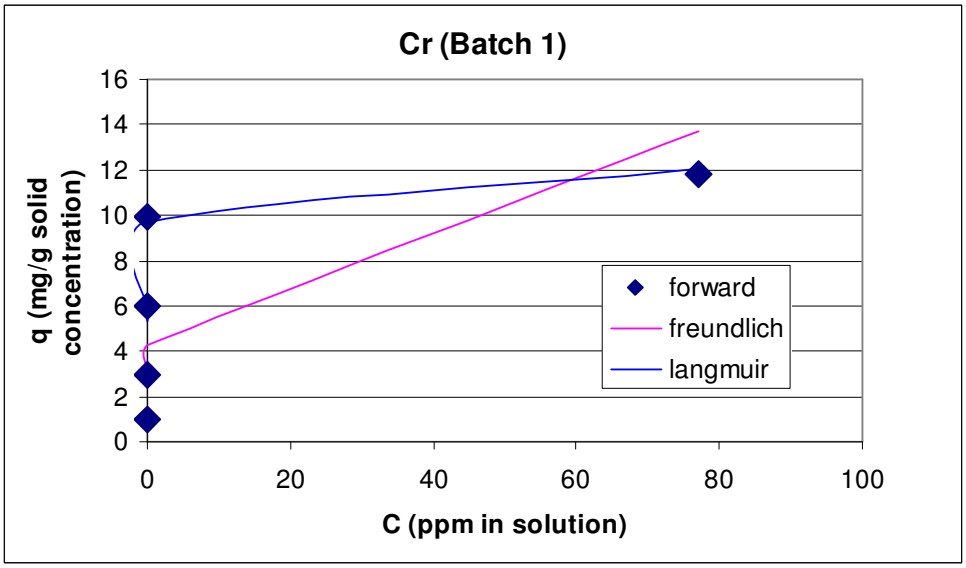


Figure 8b Chromium adsorption with second batch of zeolite

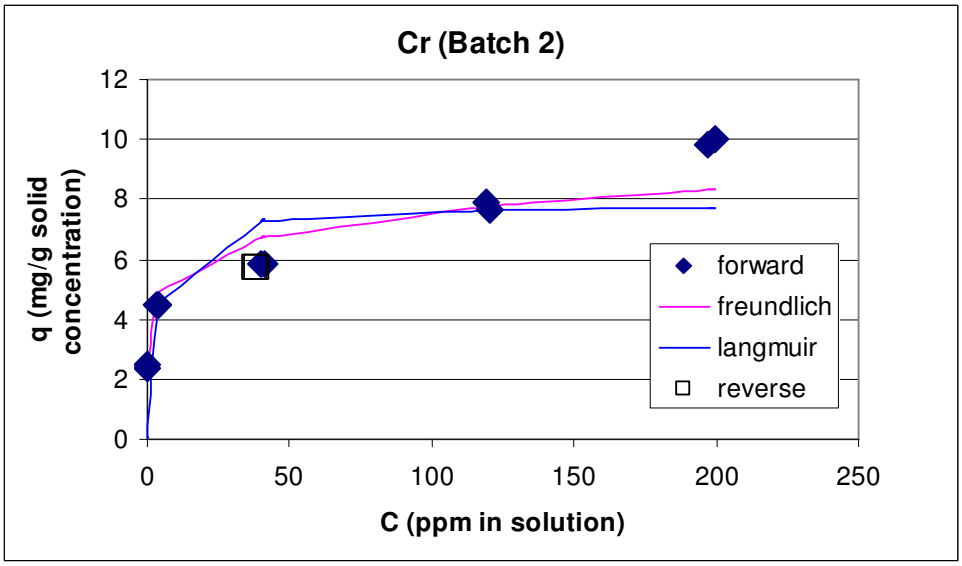


Figure 9a Cadmium adsorption with initial batch of zeolite

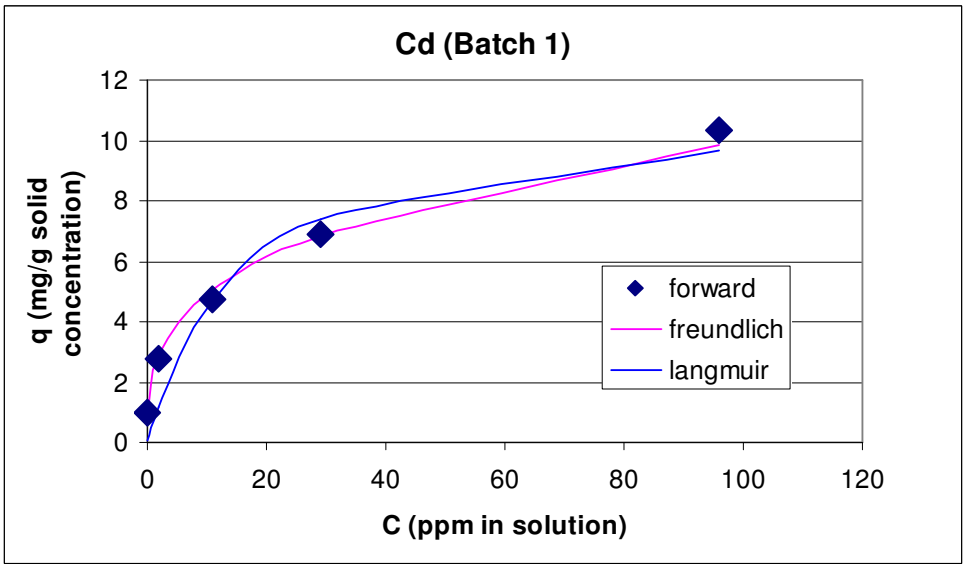
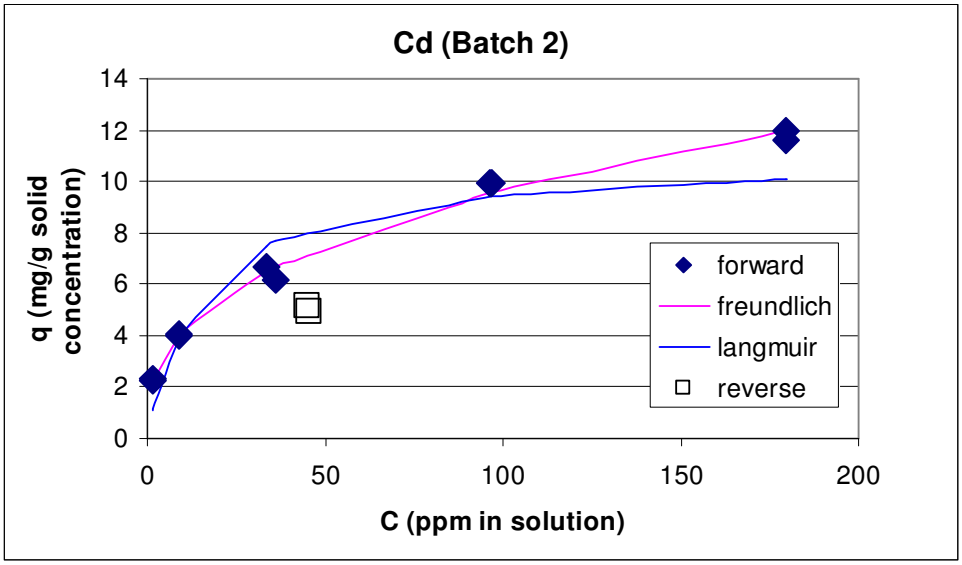


Figure 9b Cadmium adsorption with second batch of zeolite



3.3 Discussion

3.3.1 Description of isotherms

The data generated for the two batch of zeolite were compared with mathematical models of the adsorption process. For the second batch of zeolite and the more complete data sets from the fist batch (where a range of final solution concentrations were measured), it is possible to fit two of the simpler model behaviours. Both the Langmuir and Freundlich isotherms can be fitted to the data with differing degrees of success for the different cations. The true behaviour of the system probably lies somewhere between that described by the two equations. The Langmuir isotherm describes an homogenous surface where the adsorption of further ions is independent of those already adsorbed. The Freundlich isotherm describes a situation where the amount of ions already adsorbed exponential decreases the ability of further ions to become attached. The two isotherms are described mathematically in equations 1 and 2 below. Other models such as the Temkin isotherm were investigated. The assumption of the Temkin isotherm is that like Freundlich, more energy is required to adsorp each subsequent ion, but unlike Freundlich the energy increase is linear. These plots suggested the possibility of two adsorption regions of which at least one was linear, however with limited data for each isotherm it was not possible to sensibly determine the coefficients with any accuracy.

$$q = \frac{Q_{\max} K_L c}{(1 + K_L c)} \qquad \textbf{Langmuir isotherm} \qquad \text{equation 1}$$

$$q = K_f c^{\beta} \qquad \textbf{Freundlich isotherm} \qquad \text{equation 2}$$

where:
q = concentration in the solid phase
c = concentration in the liquid phase
Q_{max} = maximum solid state concentration
K_L = Langmuir equilibrium constant
K_f = Freundlich equilibrium constant
β = a constant for a given combination of adsorbent and adsorbed species

Fitting these two equations to the data plotted in figures 2-9 gives the values for the parameters of the adsorption models shown in table 3 (Langmuir) and table 4 (Freundlich), these values are used to plot the relevant curves in figures 2-9. The models found to be most applicable to each data set are summarised in table 5. For zinc and chromium neither model provides a good fit to the data and for several of the first batch results it is not possible to discriminate between the models with the information available.

Table 3 Parameters of Langmuir isotherm to fit adsorption data shown in figures 2-9

	Batch 1		Batch 2	
	K_L	**Q_{max}(mg/g)**	**K_L**	**Q_{max}(mg/g)**
NH_4	0.0412	5.7208	0.0373	8.375
Cu^{2+}	1.2056	15.5039	0.0471	11.3250
Zn^{2+}	0.2377	12.6103	0.0303	10.4384
Pb^{2+}	0.9650*	72.4637*	0.0274	48.3092
Ni^{2+}	0.385	11.1235	0.0313	10.7181
Co^{2+}	0.0630	7.2098	0.1137	5.0505
Cr^{3+}	43.5789*	12.0773*	0.3644	7.7942
Cd^{2+}	0.0653	11.2233	0.0644	10.9649

Table 4 Parameters of Freundlich isotherm to fit adsorption data shown in figures 2-9

	Batch 1		Batch 2	
	K_f	**β**	**K_f**	**β**
NH_4	0.5388	0.4791	0.6487	0.5873
Cu^{2+}	7.0372*	0.1974*	2.8307	0.2416
Zn^{2+}	5.3174	0.1850	1.3301	0.3725
Pb^{2+}	42.160*	0.8570*	11.342	0.2175
Ni^{2+}	2.359	0.2770	1.1631	0.4202
Co^{2+}	2.2387	0.2156	1.3357	0.2816
Cr^{3+}	6.4343*	0.1741*	4.1219	0.1332
Cd^{2+}	2.4021	0.3090	1.8412	0.3604

*Note Cu Pb and Cr batch 1 data included for completeness – small spread of data produces large uncertainty in isotherm parameters

Table 5 Summary table showing which of the two isotherms provides the best fit to the available data

	Batch 1	Batch 2
NH_4	Langmuir	Langmuir
Cu^{2+}	-	Freundlich
Zn^{2+}	either	either
Pb^{2+}	-	Freundlich
Ni^{2+}	either	Freundlich
Co^{2+}	Freundlich	Freundlich
Cr^{3+}	-	either
Cd^{2+}	Freundlich	Freundlich

The data in figures 2-7 and tables 3-4 are recorded in terms of the concentrations by weight; however the adsorption behaviour of the cations is as number of sites. This does not alter the fit of the models, but the exact values of distribution coefficients K_L

and K_f will be affected if concentrations are expressed as the number of millimols per gram or litre instead of the weight. This also means that the values of Q_{max} given in table 3 cannot be directly compared for the different element and are therefore recalculated in terms of millimols per gram in table 6. Although the Langmuir isotherm is an imperfect fit for many of the zeolite-cation pairings it provides a useful estimate of the maximum capacity of the zeolite samples for each cation.

Table 6 Recalculation of Q_{max} in terms of mmols/g

	Batch 1		Batch 2	
	Q_{max} mg/g	**Q_{max} mmol/g**	**Q_{max} mg/g**	**Q_{max} mmol/g**
NH_4	5.7208	0.3178	8.375	0.4653
Cu^{2+}	15.5039	0.2441	11.3250	0.1783
Zn^{2+}	12.6103	0.1927	10.4384	0.1596
Pb^{2+}	72.4637*	0.3497	48.3092	0.2334
Ni^{2+}	11.1235	0.1891	10.7181	0.1826
Co^{2+}	7.2098	0.1222	5.0505	0.0857
Cr^{3+}	12.0773*	0.2308	7.7942	0.1499
Cd^{2+}	11.2233	0.0996	10.9649	0.0976

From the data recalculated in table 6 it is possible to see that the zeolite adsorbs the same order in moles of each of the eight cations there is however a differences in the absolute amount of each element adsorbed. Although the data suggests that the order of affinity for the second batch zeolite is NH_4, Pb, Ni, Cu, Zn, Cr, Cd, Co, this should not be taken as a full description of the performance of the materials as cation adsorbents, as it can be seen from figures 2-9 that the langmuir model does not fully describe the results obtained in this study. A similar trend can be constructed for the first batch with generally higher values of Q_{max} for the metal cations, however due to the bunched nature of the data points at low solution concentrations the fit of the models are not as reliable and so these results should be taken with caution. The generally better performance of the first batch of zeolite with respect to the metal cations can however be seen by simple comparison of the final concentrations of the initially 100 and 200ppm solutions which are lower with concomitantly higher solid phase concentrations. The levels of absorbance seen, for both batches, are however of the order seen in other studies of the behaviour of natural zeolite or clinoptilolite material in similar tests [1,2,3].

The explanation for the different behaviour of the two batches cannot be determined from the data gathered during this study. The improved adsorption of ammonium whilst reducing for the metals from the first batch to the second suggests that it is more than just a change in the proportion of one ion-exchanging phase. The deposit from which the two batches are samples is believed to be largely clinoptilolite, however other minerals which may have a slight ion-exchange or even ion-absorbing capacity may be present. It may also be possible that in response to elements present in the zeolite that some of the cations added precipitate or are otherwise removed from solution. The behaviour of the system as a non-ideal exchanger is further suggested by the reverse points for two of the cations. In response to an excess of sodium ions, the desorption of cadmium and ammonium is greater than would be expected for a pure ion-exchange medium, whilst the response of the other six cations falls on or close to the forward isotherm.

4. Predictive modelling and column trials

4.1 Methodology

The column experiments were carried out by pumping a solution of known concentration through a packed column (total volume 18ml) using a peristaltic pump. Fractions of either 5 or 10ml were then collected from the output of the column with a fraction collector. The column experiment was carried out using ammonia rather than copper as the exchanging cation due to the better quality of supporting data gathered during this investigation. Analysis of ammonia was by the Indophenol method.

The column was packed with zeolite material >150μm and <900μm, the use of coarser material than that used for the batch tests was due to the fine materials initially supplied (30-50μm) passing through course filters and clogging fine filters. The 150-900μm material is a slightly less efficient ion exchanger than the fines, with the former adsorbing 5.7 mg NH_4 per gram from a 100ppm solution in comparison to the 6.4 mg NH_4 per gram for the latter. The use of larger particles is also kinetically less than ideal, but probably represents a better approximation of how these materials react in practice. The particles were graded using a 150μm sieve to remove any fine particulates which would clog the system; the zeolite was then packed into the column and washed in-situ with distilled water, until all remaining dust had been removed.

Two column experiments were carried out, the mass of zeolite used and column bed volumes are given in table 7. The peristaltic pump was set at approximately 5 pore volumes per hour for both experiments. Two different concentrations of NH_4 were used to attempt to validate some of the assumptions required for model fitting. The model fits are calculated by PHREEQCI software from the United States Geological Survey, modelling in advection mode only. This model splits the column into cells and calculates the exchanger and solution composition as each cell reaches equilibrium. The solution is then shifted on to the adjacent cell and allowed to come to equilibrium with the ion exchanger present in that cell. As long as local equilibrium is assumed the column should behave as a series of infinitely small cells. In practice for a column of this size the model requires only 40 cells before increasing the number yields no perceivable difference.

Table 7 : Solution concentration, mass of ion-exchanger and pore volume

Solution concentration	Zeolite Mass	Pore Volume
500 ppm	20.27g	8.875 ml
250 ppm	18.57g	8.138 ml

4.2 Single element model

The single element model was based on a purely calcium ion exchanger. A range of total ion-exchange capacities were used starting at Q_{max} (from Langmuir isotherm for ammonia) for the zeolite powder and rising to give the best fit with the onset of breakthrough. This model proved inadequate, as the curvature of the onset slope was dependant on a small number of cells being used in the calculation (between 2 and 4). This selection of the number of cells is entirely arbitrary and of no practical use in predicting column behaviour. We have therefore discounted this model in favour of a more complex multi-element prediction.

4.3 Multi-element model

A multi-element model was devised where the ion-exchange capacity of the theoretical column was made up of sodium, calcium and magnesium exchanger in the ratio observed in the exchangeable test carried out for Euremica previously. This model proved a significantly better fit for the onset of breakthrough.

The total ion exchange capacity was varied to give a good fit to the observed data. Figures 10 and 11 show the fit for the 500 and 250 mg/l columns respectively, with varieties of ion exchange capacity ranging from Q_{max} until an adequate fit is observed.

Figure 10: Model fits and experimental data for 500ppm column

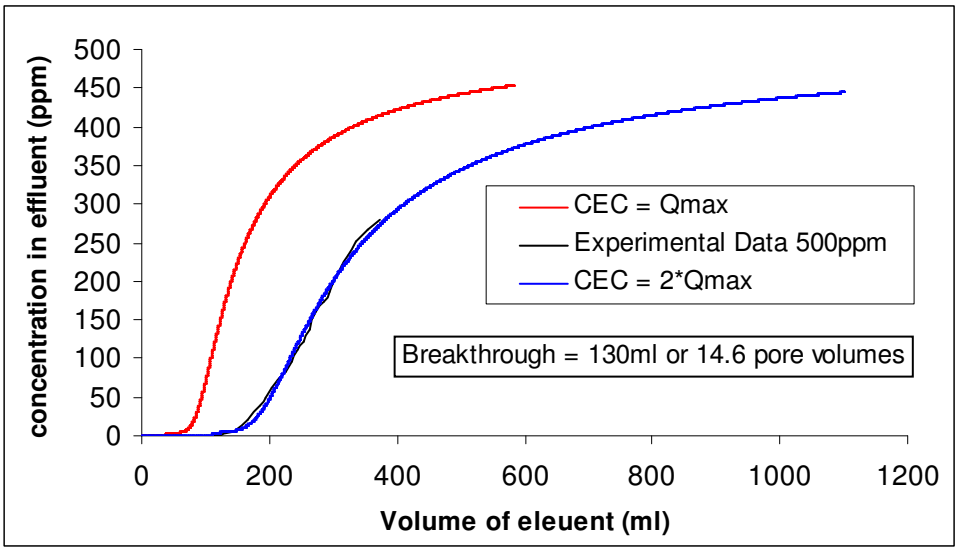
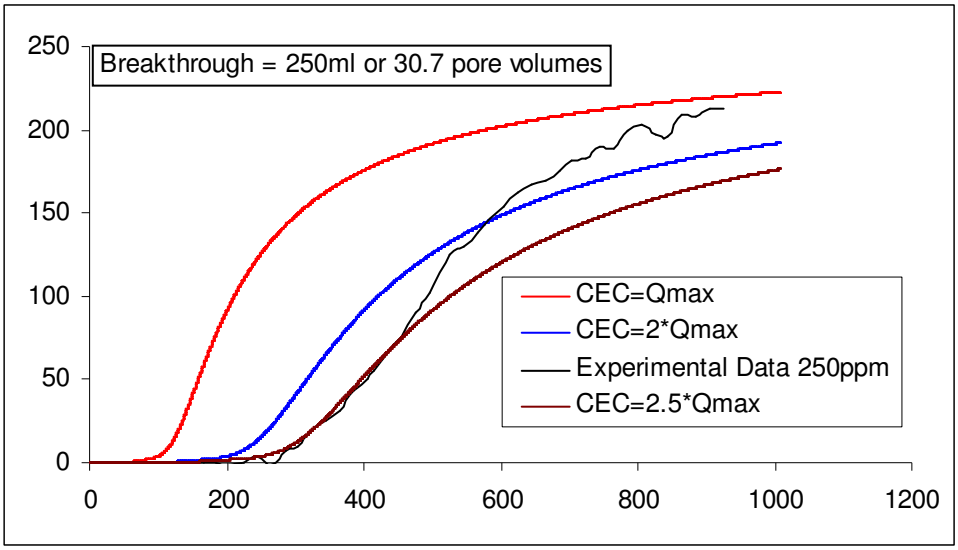


Figure 11: Model fits and experimental data for 250ppm column



These figures show that the prediction of onset is difficult. A higher value of CEC is required to predict the onset of breakthrough than is predicted by the available ion-exchange sites at equilibrium given by Q_{max}. This would indicate that some sites are activated for exchange by the effluent from the column, which is in effect pre-treating the zeolite with sodium then calcium solution before adsorption of ammonia. It is also clear that even this simple multi-element model does not predict the whole pattern of

breakthrough as the 250ppm experimental data deviates considerably from the predicted model. This is probably due to the number of ion-exchange sites changing with elution of the column.

Further investigation would be required before anything other than a conservative estimate of the onset of breakthrough could be predicted. However this experiment has shown that the performance of the zeolite material is better than has been predicted by simple batch experiments.

5. Conclusions

- The two different zeolite samples supplied appear to show different behaviour in response to the different cations.

  The second batch shows a greater ability to adsorb ammonium with a lower affinity for all of the metal species. Even allowing for the limited spread of data from the first batch of zeolite it is clear from a simple comparison of the results for the initially 100 and 200 mg/l solutions that a greater proportion was removed by the first sample than seen for the subsequent material. A full explanation of this behaviour is not possible with the information currently available.

- The expected capacity of the two materials for the cations investigated are summarised in table 8.

Table 8. Summary of the maximum solid concentrations expected for the two batches of zeolite based upon the highest measured level and estimated Q_{max}.

	Range of maximum solid adsorption capacities (mg/g)	
	Batch 1	Batch 2
NH_4	5-5.7	6.2-8.4
Cu^{2+}	13.8-15.5	11.3-11.4
Zn^{2+}	12.6-12.7	9.5-10.4
Pb^{2+}	*	48.3-56.7
Ni^{2+}	10.0-11.1	10.7-11.1
Co^{2+}	6.7-7.2	5.1-5.4
Cr^{3+}	*	7.8-9.9
Cd^{2+}	10.4-11.2	11.0-11.8

* Insufficient data to provide sensible estimate however conservative estimate may be made using data from batch 2.

- Differences in the precise mineralogical composition of the two samples may be an important factor.

  The deposit the material is derived from is believed to be largely clinoptilolite, however other minerals, such as clays, may be present which also have adsorption or ion-exchange capacities and contribute to the overall behaviour of the samples used in this study.

- The system is not behaving as an single site ion-exchanger as would be expected for a pure single phase zeolitic material

This is illustrated by the fact that two of the reverse isotherm points (Cd and NH_4) do not fall on the forward isotherm . Also the fact that the data does not fit precisely to the adsorption isotherm models suggests that either more than one exchanger is present or more than one type of exchange site exists, giving rise to a behaviour which is a composite of different isotherms.

- The performance of the zeolite in the column trials is better than that which would be expected from the initial batch isotherm

This is encouraging as the coarser material used would be expected to show a less efficient removal than the very fine material used in the batch trials. This suggests that it may be possible to activate the zeolite and thereby enhance its performance prior to use, however further trials would be necessary to confirm this phenomena, which has also been previously reported in other studies[2], and develop an optimum pre-treatment step if applicable.

References

1. Langella, A. *et al.,* Microporous and Mesoporous Materials **37** pp337-343 (2000)
2. Cincotti, A. *et al.,* Chemical Engineering Journal **84** pp275-282 (2001)
3. Inglezakis, V.J. *et al.,* Water Reseach **36** pp2784-2792