Articles

Comparison of Amberlite IRC-748 Resin and Zeolite for Copper and Ammonium Ion Exchange

Kathryn A. Mumford,[†] Kathy A. Northcott,[†] David C. Shallcross,[†] Ian Snape,[‡] and Geoff W. Stevens*[,†]

Particulate Fluids Processing Centre, Department of Chemical and Biomolecular Engineering, University of Melbourne, Melbourne, Victoria 3010, Australia, and Environment, Protection and Change Program, Australian Antarctic Division, Channel Highway, Kingston, Tasmania 7050, Australia

A sodium-form chelating ion-exchange resin, Amberlite IRC-748, and a natural zeolite were investigated for the exchange of copper and ammonium ions from aqueous solutions at three temperatures ((4.0, 20.0, and 40.0) ± 0.2) °C. Maximum exchange capacities were determined, and a temperature-dependent, semi-empirical thermodynamic ion exchange model used to describe the ion exchange behavior of the binary systems. It was found that the model selected fitted the data well for both systems. The resin was significantly more selective toward copper compared to zeolite, and the zeolite preferred ammonium to copper cations. Both systems exhibited an increase in selectivity toward copper or ammonium with an increase in temperature.

Introduction

A legacy of past poor waste management practices associated with the operation and maintenance of Antarctic Research Stations has resulted in numerous contaminated sites. When planning field remediation strategies for Antarctica, a number of issues must be considered. Field teams need to select robust, compact equipment and materials to allow for transport to remote locations and harsh weather conditions, and processes need to operate at low to freezing temperatures. The most important consideration is that any item used or installed needs to have no long-term adverse impact on the environment. Because of these special requirements, there is a need to develop new approaches and technologies to enable simple, reliable, and inexpensive wastewater treatment systems.[1]

Although there are many technologies that may be adapted for use in these environments, ion exchange has been identified as an appropriate technology for water treatment. There are a wide variety of materials available to perform ion exchange functions, including synthetic resins and zeolites. Synthetic resins can be designed to have superior ion exchange properties, but they are not necessarily appropriate for every circumstance. For instance, synthetic resins are costly, may be unable to withstand extreme cold, and may pose a risk to the Antarctic environment, so their use for in-ground treatments warrants careful consideration. Zeolites by contrast are cheap, robust, and relatively harmless in the environment. The Australian Antarctic Division has used a chelating ion-exchange resin in a portable wastewater treatment plant[2] and zeolite as a controlled-release nutrient medium to promote degradation of petroleum hydrocarbons.[3] While these design decisions have resulted in good outcomes, this paper aims to investigate the comparative performance of these two materials over a wide temperature range, through use of a recently developed ion exchange model.[4]

Experimental Material, Apparatus, and Procedures

Resin, Zeolite, and Solutions. Two ion exchange media were studied in the experimental program. The first was a commercially available chelating resin, Amberlite IRC-748, and the second was a natural zeolite from the St. Cloud mine, Winston, New Mexico. Amberlite IRC-748 is an iminodiacetic acid (IDA) chelating cation exchange resin on a macroporous styrene divinylbenzene matrix and has a particularly high selectivity for transition metals. Zeolites are alumino-silicates possessing three-dimensional frameworks of linked silicon−aluminum−oxygen tetrahedra.[5] The aluminum present within the zeolite framework results in a net negative charge which is balanced by loosely held cations located throughout the channel network. A mineralogical analysis of St. Cloud mine zeolite has been conducted elsewhere.[6] The results indicate that it comprises 74 % clinoptilolite, 10 % feldspar, 10 % quartz and cristobalite, 5 % smectite, and 1 % illite. The copper chloride, sodium chloride, ammonium chloride, and potassium chloride used were of analytical grade (Sigma Aldrich), and MilliQ water was used for all solution preparation.

Preconditioning Process. Before use, the resin and zeolite samples were converted into the sodium-form. A second batch of zeolite was converted into the ammonium-form. The resin was converted into the sodium-form by first washing it of any water-insoluble residues using MilliQ water and then conditioned into the hydrogen form through consecutive washing with 0.5 mol·L^{-1} hydrochloric acid. It was then transferred into the sodium form through washing with a 0.5 mol·L^{-1} sodium hydroxide solution, followed by rinsing with MilliQ water. The natural zeolite was conditioned into the sodium or ammonium form by consecutively washing approximately 50 g with a concentrated (2 mol·L^{-1}) chloride solution under agitation from

---

* Corresponding author. E-mail: gstevens@unimelb.edu.au.
[†] University of Melbourne.
[‡] Australian Antarctic Division.

10.1021/je7006428 CCC: $40.75

Table 1. Maximum Exchange Capacity of Exchangers in Systems Studied

temperature (°C)	Cu^{2+} on Na−zeolite (meq·g (dry)$^{-1}$)	Cu^{2+} on Na−IRC 748 (meq·g (dry)$^{-1}$)	NH_4^+−zeolite (meq·g (dry)$^{-1}$)
4	0.29	5.4	0.83
20	0.35	5.4	−
25	−	−	0.83
40	0.35	5.4	−

Table 2. Effective Ionic and Hydrated Ion Radii of Selected Cations and Energy of Hydration[19,20]

cation	ion radius (nm)	hydrated ion radius (nm)	enthalpy of hydration (kJ·mol^{-1})
Cu^{2+}	0.070	0.419	−2100
Na^+	0.095	0.358	−405
NH_4^+	0.148	0.331	−385

Table 3. Single Salt Pitzer Model Parameters

compound	$\beta^{(0)}_{Ma}$	$\beta^{(1)}_{Ma}$	C^{ϕ}_{Ma}
$CuCl_2$[a]	0.2966	1.3910	−0.03602
NH_4Cl[b]	13.1590	11.0178	−0.913034
273.15 < T (K) < 373.15	$+0.00261316T$	$+0.00523542T$	$-0.000145757T$
	$-436.157/T$ $-2.18043 \ln(T)$	$-212.168/T$ $-2.04936 \ln(T)$	$+32.8062/T$ $+0.148049 \ln(T)$

[a] Ref 21. [b] Ref 22.

Table 4. Mixed Electrolyte Pitzer Model Parameters

A	B	X	θ_{AB}	Ψ_{ABX}
Cu	Na	Cl	0[a]	−0.014[a]
NH_4	Na	Cl	0.00436[b]	−0.0031[b]

[a] Ref 21. [b] Ref 23.

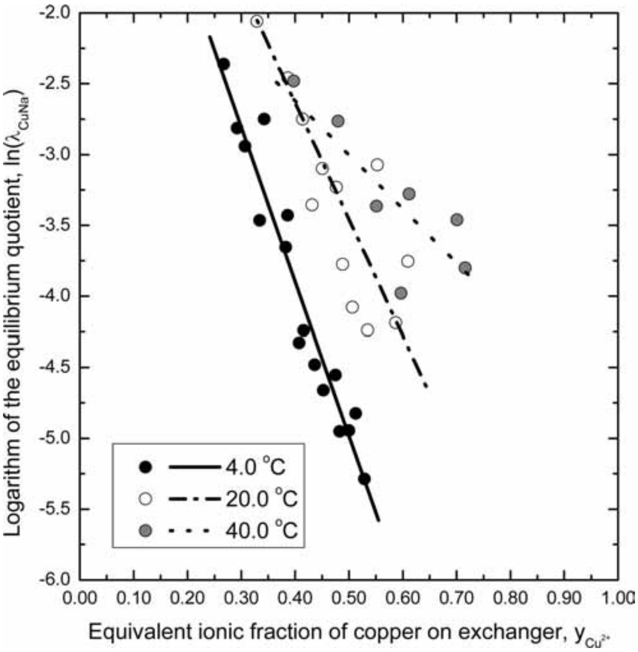

Figure 1. Logarithm of equilibrium quotient, λ, versus ionic fraction of copper of the exchanger, at three different temperatures for the sodium−copper−zeolite system at 100 mg·L^{-1} copper concentration.

a rotary platform shaker at 150 rpm for 72 h. The exchanging solution was replaced every 24 h. The supernatant was drained, and the sample was rinsed three times with MilliQ water to remove excess salt, dried at 105 °C, and equilibrated with the atmosphere.

Maximum Exchange Capacities. The maximum exchange capacities and binary equilibria relationships of the preconditioned resin and zeolite were investigated. Preliminary kinetic studies were performed to determine when batch test system equilibrium was attained: three days (72 h) were found to be sufficient for all the exchange systems studied.

To determine the maximum copper exchange capacity of the resin and zeolite, the media were contacted with copper chloride solution for 72 h. Tests were conducted by weighing 0.02 g of resin or 1.0 g of zeolite into 250 mL flasks. Following this, 100 mL of copper chloride solution, at one of three concentrations [(100, 250, and 500) mg·L^{-1} as copper], was added to Erlenmeyer flasks and gently agitated at 100 rpm and at the appropriate temperature for 72 h. The copper concentrations in the initial and final solutions were analyzed by Atomic Adsorption Spectrophotometry (AAS). The copper capacity was calculated by plotting the equilibrium concentration of copper on the exchanging material with respect to the equilibrium concentration of the copper in solution. The result is a straight line through the data at constant solid phase concentration which corresponds to the copper capacity of the exchanging material. This process was completed in triplicate to verify the reproducibility of results. The results are found in Table 1.

The maximum ammonium exchange capacity was determined by weighing approximately 1.0 g of ammonium form zeolite into a 250 mL Erlenmeyer flask. An amount of 100 mL of 2 mol·L^{-1} potassium chloride was added to the flasks, and they were gently agitated at 100 rpm for 72 h. The initial and final ammonium concentrations were determined with a Cary UV−Vis spectrophotometer, and the maximum ammonium exchange capacity per gram of zeolite was determined.

Moisture Content. The moisture content of the exchange media at every analysis stage was determined so that all results may be presented on a dry mass basis. A sample of the exchange media was weighed and placed into an oven at 105 °C for 24 h. The media was then reweighed upon removal from the oven. The moisture content was determined from the difference in mass before and after heating. After heating, the sample was discarded.

Binary Equilibrium Experiments. The binary equilibrium experiments were performed by placing resin or zeolite of known form and mass into a 250 mL Erlenmeyer flask with precisely 100.0 mL of copper/ammonium chloride solution (nominal concentrations of (25, 50, and 100) mg·L^{-1} copper concentration, 0.4 mol·L^{-1} ammonium concentration) and gently agitating for 72 h. At the conclusion of this period, the solution was decanted from the exchanger, and the concentration of analyte was measured. Once the equilibrium composition of the solution phase was determined, the equilibrium composition of the exchanger or resin phase was inferred by use of a simple material balance. The tests were conducted at a variety of temperatures, ((4.0, 20.0, 25.0, and 40.0) ± 0.2) °C.

Results and Discussion

Total exchange capacity is the number of equivalent ionogenic groups in the material. However, not all of these sites are available for exchange due to issues such as the exclusion of cations through molecular sieve processes or exchange sites being present at inaccessible areas of the material framework. Maximum exchange capacities (MEC) are experimentally measured and represent the total number of exchange sites available to a particular ion.

The MEC for the resin and zeolite materials for different exchanging cations are presented in Table 1, and these results

Table 5. Equilibrium Constants and Interaction Parameters Obtained in Study

system	IRC−748, Na−Cu			zeolite, Na−Cu			zeolite, Na−NH_4	
temp	4 °C	20 °C	40 °C	4 °C	20 °C	40 °C	4 °C	25 °C
K_{AB}	0.219	0.332	0.442	0.00553	0.00898	0.0242	37	54
Λ_{AB}	0.703	0.941	1.178	25	22	17	1.2	0.8
Λ_{BA}	1.42	1.06	0.849	6.0	0.50	0.040	0.40	1.5

are comparable to those found by other researchers.[7–10] The maximum copper exchange capacity of the synthetic resin was significantly greater than for the natural zeolite. For the zeolite system, the maximum ammonium exchange capacity is also significantly higher than that for copper. Comparatively lower zeolite heavy metal cation maximum exchange capacity, as compared to other cations, is a trend found widely in the literature.[7] It is generally believed that this is due to the steric exclusion of cations entering the zeolite framework channels, where the majority of the ion exchange processes occur. Cation exclusion is related to the relative sizes of the channel and the hydrated cation.

The zeolite mineralogical analysis indicated that St. Cloud mine zeolite was predominately clinoptilolite. Clinoptilolite has the ideal formula of (Ca, Na_2, K_2)(Al_6SiO)·$24H_2O$, and its structural framework contains a network of channels defined by two eight-ring pores, of dimensions 0.26 × 0.47 nm and 0.33 × 0.46 nm, and one ten-ring pore, of dimensions 0.30 × 0.76 nm. Note that the hydrated sizes of ammonium and copper cations (Table 2) are close to the channel dimensions of the zeolite, and the hydrated copper ion size is approximately 20 % larger than sodium and ammonium radii. These relative sizes may in part explain the variation in the observed exchange capacities.

Temperature also appears to have an effect on the maximum copper exchange capacity of zeolite, with capacity decreasing with decreasing temperature. This effect has been observed

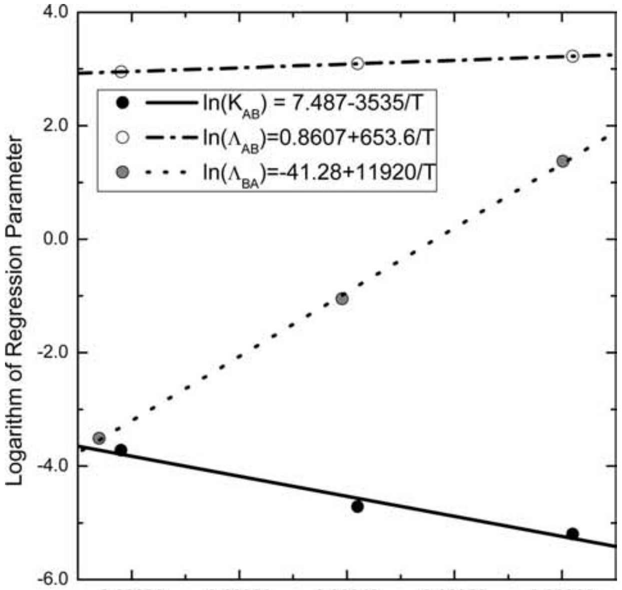

Figure 2. Regression of model parameters with temperature, K_{AB} (equilibrium constant) and Λ_{AB}, Λ_{BA} (Wilson interaction parameters), for the sodium−copper−zeolite exchange system.

Table 6. Arrhenius Relations for Equilibrium Constant and Interaction Parameter

system	IRC-748, Na−Cu	zeolite, Na−Cu	zeolite, Na−NH_4
ln K_{AB}	$-1683/T + 4.582$ ($r^2 = 0.9821$)	$7.487 - 3535/T$ ($r^2 = 0.9718$)	$-1501/T + 9.029$
ln Λ_{AB}	$-1239/T + 4.135$ ($r^2 = 0.9893$)	$0.8607 + 653.6/T$ ($r^2 = 0.9999$)	$4318/T - 15.41$
ln Λ_{BA}	$1238/T - 4.135$ ($r^2 = 0.9894$)	$-41.28 + 11920/T$ ($r^2 = 0.9995$)	$-2471/T + 8.697$

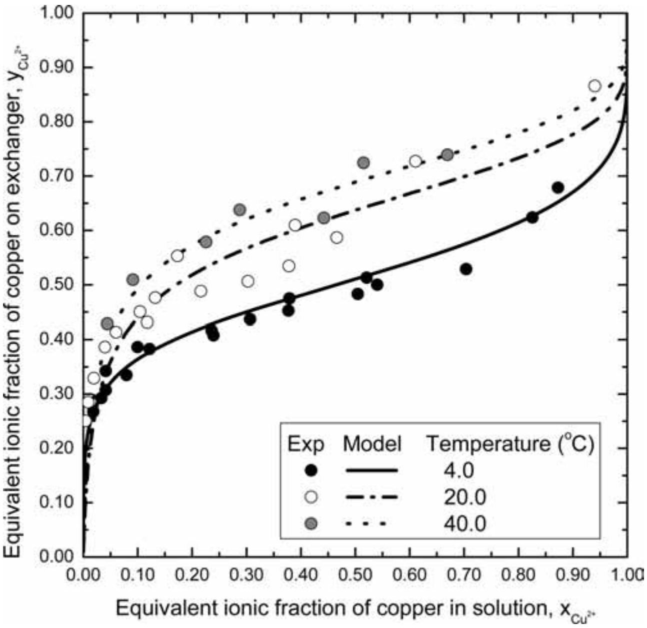

Figure 3. Application of the semiempirical thermodynamic model to predict binary isotherms for copper−sodium on zeolite at three temperatures and an initial exchanging concentration of 100 mg·L^{-1}.

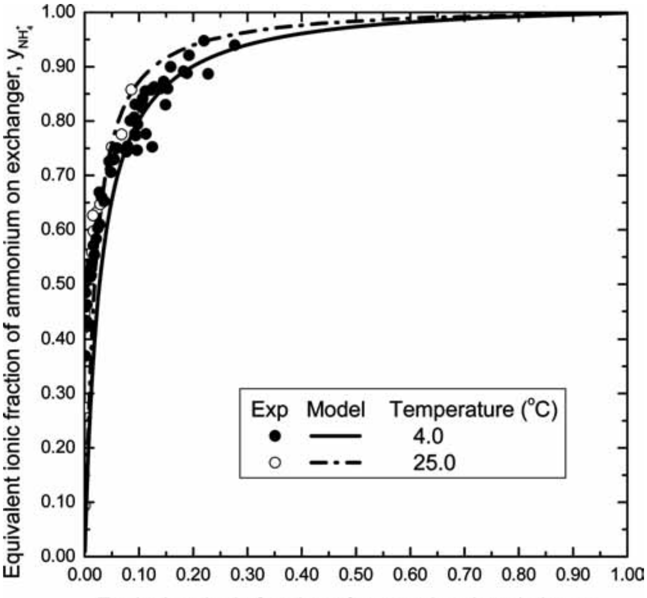

Figure 4. Application of the semiempirical thermodynamic model to predict binary isotherms for ammonium−sodium on zeolite at two temperatures and an initial exchanging concentration of 0.4 mol·L^{-1}.

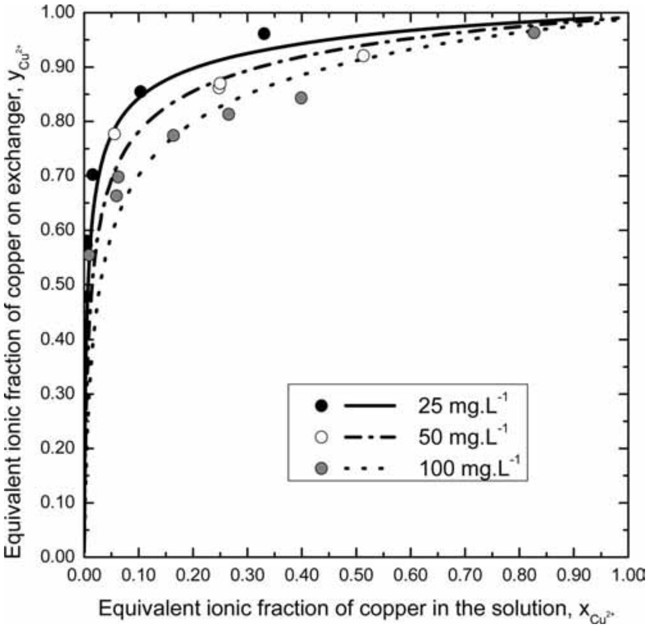

Figure 5. Application of the semiempirical thermodynamic model to predict binary isotherms for copper−sodium on resin at three exchanging solution concentrations and a temperature of 4 °C.

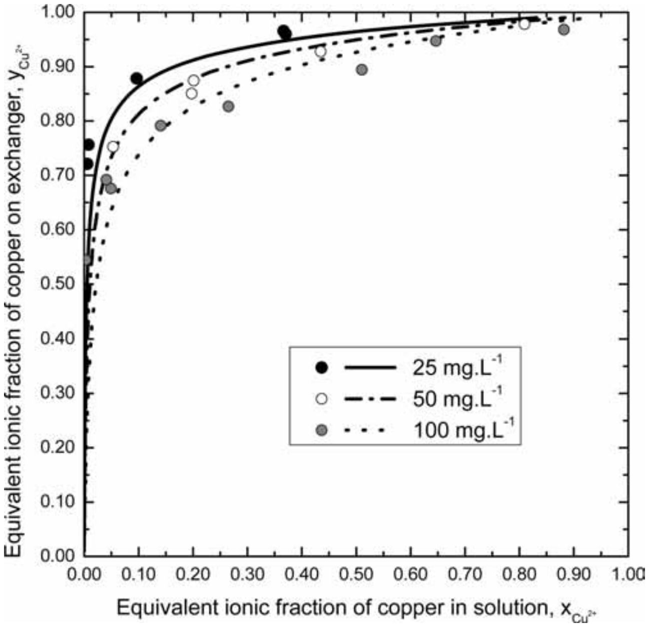

Figure 6. Application of the semiempirical thermodynamic model to predict binary isotherms for copper−sodium on resin at three exchanging solution concentrations and a temperature of 40 °C.

previously, and it has been commented that it may be due to an increase in the effective size of the ions caused by an increase of the ion hydration shell, and hence effective radius, with a decrease in temperature.[11,12]

Binary Equilibria Modeling. The analysis of binary equilibria of the systems described was conducted whereby the exchanger phase concentration of the exchanging ions is linked to the solution phase concentration by the equilibrium model developed by Mehablia et al. and adapted by Mumford and coworkers[4] to incorporate the effect of temperature. Briefly, in this technique, the exchange of two ions between a solution phase and an exchanger phase is represented by the stoichiometric equation

$$z_b A^{\pm z_a} + z_a \overline{B^{\pm z_b}} \rightleftharpoons z_b \overline{A^{\pm z_a}} + z_a B^{\pm z_b} \qquad (1)$$

where z_a and z_b are the valencies of ionic species A and B, respectively, and the underline denotes that the ion is in the exchanger phase. The equilibrium constant for such an exchange is written in terms of the activities of the ions.

$$K_{AB} = \left(\frac{\overline{a_A}}{a_A}\right)^{z_b} \cdot \left(\frac{a_B}{\overline{a_B}}\right)^{z_a} \qquad (2)$$

The solution phase activity coefficients are calculated by the Pitzer model[14,15] using free ion concentrations as determined by the technique proposed by Kester and Pytkowicz.[16] The exchanger phase activity coefficients are calculated via the Wilson model and the equilibrium constant by the approach of Gaines and Thomas.[17] Temperature dependence is incorporated

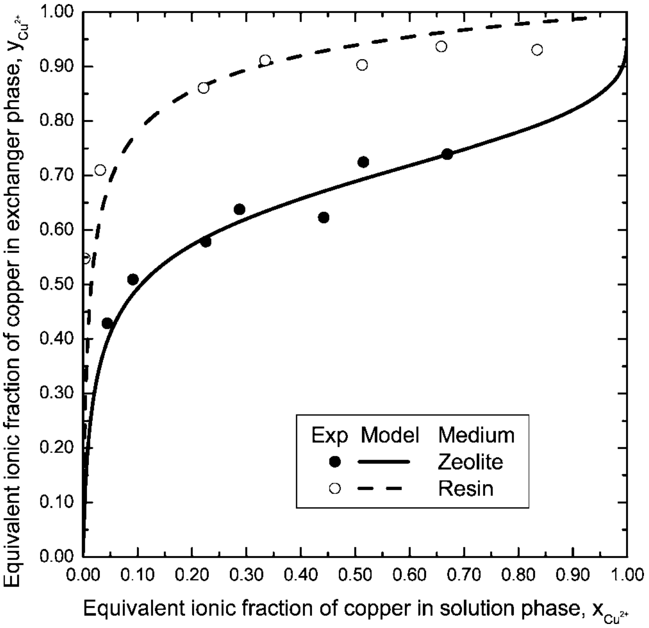

Figure 7. Comparison of zeolite and resin for copper uptake at an initial exchanging concentration of 100 mg·L^{-1} and at 40 °C.

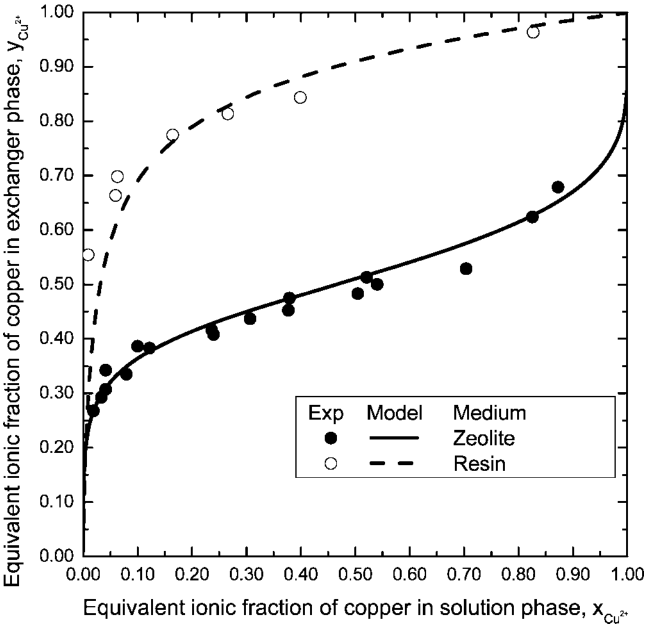

Figure 8. Comparison of zeolite and resin for copper uptake at an initial exchanging concentration of 100 mg·L^{-1} and at 4 °C.

through use of the Gibbs free energy function. This model is described more fully elsewhere.[4]

The Pitzer model parameters required to calculate the activity of the solution phase in this study are presented in Tables 3 and 4. As stated, the equilibrium constant is determined using the method of Gaines and Thomas. In this method, the equilibrium constant is found through the integration of the logarithm of the equilibrium quotient, λ_{AB}, against the equivalent ionic fraction in the exchanger phase, as presented in eqs 3 and 4.

$$\ln K_{AB} = (z_B - z_A) + \int_0^1 \ln(\lambda_{AB})\mathrm{d}y_A \qquad (3)$$

where

$$\lambda_{AB} = \left(\frac{y_A}{\gamma_A x_A}\right)^{z_B}\left(\frac{\gamma_B x_B}{y_B}\right)^{z_A} \qquad (4)$$

An example of the relation to be integrated is shown in Figure 1. This figure also indicates a strong dependence of the equilibrium quotient and hence the equilibrium constant on system temperature. This is further illustrated by the calculated equilibrium constant values presented in Table 5. Similar plots may be produced for the ammonium−sodium−zeolite and copper−sodium−resin systems.[18]

The equilibrium constants presented in Table 5 show that copper exchange onto the resin is significantly more favorable than for copper onto the zeolite. Additionally, the selectivity of the zeolite for ammonium is greater than for copper. This result agrees with the work of numerous other authors such as Cinotti,[7] who found the selectivity series of clinoptilolite to be

$$\mathrm{Pb}^{2+} > \mathrm{NH_4}^{+} > \mathrm{Cd}^{2+}, \mathrm{Cu}^{2+}, \mathrm{Sr}^{2+} > \mathrm{Zn}^{2+} > \mathrm{Co}^{2+} \qquad (5)$$

The selectivity series of a zeolite ion exchanger is the result of various factors. One factor is the geometrical sieving effect as discussed previously; the other is the ion hydration energies. The lower the hydration free energy of an ion, the greater ease with which its water of hydration may be shed. The ion with the higher free energy of hydration will therefore remain in the solution phase. Copper, as shown in Table 2, has a significantly higher enthalpy of hydration and so will preferentially be in the solution phase as compared to sodium and ammonium.

As described in previous studies,[4] Arrhenius-style relations may be regressed to relate the equilibrium constant of a system to the temperature at which the ion exchange process takes place. The graphical and tabular representation of this is presented in Figure 2 and Table 6, respectively. Both representations show the data points fitting the regressed equation very well. This high correlation enables the regressed equation to be used for subsequent ion exchange equilibria prediction with a relatively high degree of confidence.[4]

The next stage of this technique is the regression of the Wilson Binary interaction parameters (Λ_{AB}, Λ_{BA}). This procedure was conducted for each system, solution concentration, and temperature. Once again, an Arrhenius style of relation was found (Figure 2 and Table 6). The temperature-dependent regressions for the interaction parameters and equilibrium constants were then used to find the equilibrium constant and the exchanger phase activities to be substituted into eq 2 to form the ion exchange predictions. Figure 3 shows the ion exchange data and prediction of the copper−sodium zeolite system at 100 $\mathrm{mg \cdot L^{-1}}$ and three temperatures. The model is shown to successfully predict the increase in selectivity of the resin for copper with an increase in temperature. The model also adequately predicts the relatively small effect of temperature on the ion exchange equilibria of the sodium−ammonium−zeolite system presented in Figure 4.

In addition to predicting the effect of system temperature, the model also predicts the effect of variations in initial solution concentration, shown in Figures 5 and 6. These figures show the shift in the equilibria curves when the copper solution concentration increases from (25 to 100) $\mathrm{mg \cdot L^{-1}}$. A comparison of the ion exchange equilibria for copper uptake of the zeolite and the resin at (40 and 4) °C is presented in Figures 7 and 8. These graphs clearly show the superior selectivity of the resin for copper as opposed to zeolite which was indicated by the values of the equilibrium constants presented in Table 5.

Conclusions

The temperature-dependent behavior of three binary systems (Cu−Na−resin, Cu−Na−zeolite, Na−$\mathrm{NH_4}$−Zeolite) was investigated using the chelating cation exchange resin Amberlite IRC-748 and a natural clinoptilolite. A semi-empirical thermodynamic model incorporating temperature dependence showed good agreement with experimental equilibrium data for all system concentrations and temperatures investigated. The resin was found to have a higher selectivity for copper than the natural zeolite. The zeolite was found to have a higher selectivity for ammonium than copper.

Acknowledgment

The authors would like to thank Jeremy Lane, Salin Suralertrungsun, and Teeratas Krungkaew, University of Melbourne, for their assistance with the ion exchange experiments.

Literature Cited

(1) Stark, J. S.; Snape, I.; Riddle, M. J. Abandoned Antarctic waste disposal sites: Monitoring remediation outcomes and limitations at Casey Station. *EMR* **2006**, *7*, 21–31.

(2) Woodberry, P.; Stevens, G.; Northcott, K.; Snape, I.; Stark, S. Field trial of ion-exchange resin columns for removal of metal contaminants, Thala Valley Tip, Casey Station, Antarctica. *Cold Reg. Sci. Technol.* **2007**, *48*, 105–117.

(3) Van Stempvoort, D.; Biggar, K.; Filler, D. M.; Johnson, R. A.; Armstrong, J.; Snape, I.; Mumford, K. A.; Bainbridge, S.; Barnes, D. C.; Schnable, W. Emerging Technologies. In *Bioremediation of petroleum hydrocarbons in cold regions*; Filler, D. M., Ed.; in press; pp 212−230.

(4) Mumford, K. A.; Northcott, K. A.; Shallcross, D. C.; Stevens, G. W.; Snape, I. Development of a Two Parameter Temperature Dependant Semi-Empirical Thermodynamic Ion Exchange Model using binary equilibria with Amberlite IRC 748 resin. *Ind. Eng. Chem. Res.* **2007**, *46*, 3766–3773.

(5) Dyer, A. Zeolites. In *Encyclopaedia of Materials: Science and Technology*; Elsevier Science: New York, 2001; pp 9859−9863.

(6) Bowman, R. S.; Sullivan, E. J.; Li, Z. Uptake of cations, anions, and nonpolar organic molecules by surfactant-modified clinoptilolite-rich tuff. In *Natural zeolites for the Third Millennium*; Colella, C., Mumpton, F. A., Eds.; De Frede Editore: Naples, 2000; pp 287−297.

(7) Cincotti, A.; Lai, N.; Orru, R.; Cao, G. Sardinian natural clinoptilolites for heavy metals and ammonium removal: experimental and modelling. *Chem. Eng. J.* **2001**, *84*, 275–282.

(8) Woinarski, A. Z.; Snape, I.; Stevens, G. W.; Stark, S. C. The effects of cold temperature on copper ion exchange by natural zeolite for use in a permeable reactive barrier in Antarctica. *Cold Reg. Sci. Technol.* **2003**, *37*, 159–168.

(9) Cooney, E. L.; Booker, N. A.; Shallcross, D. C.; Stevens, G. W. Ammonia removal from wastewaters using natural Australian zeolite. I. Characterization of the zeolite. *Sep. Sci. Technol.* **1999**, *34*, 2307–2327.

(10) Muraviev, D.; Gonzalo, A.; Valiente, M. Ion exchange on resins with temperature responsive selectivity. I. Ion exchange equilibrium of Cu^{2+} and Zn^{2+} on iminodiacetic and aminomethylphosphonic resins. *Anal. Chem.* **1995**, *67*, 3028–3035.

(11) Tagami, L.; Santos, O. A. A.; Sousa-Aguiar, E. F.; Arroyo, P. A.; Barros, M. A. NaY and CrY zeolites ion exchange. Thermodynamics. *Acta Sci.* **2001**, *23*, 1351–1351.

(12) Biskup, B.; Subotic, B. Removal of heavy metal ions from solutions by means of zeoliltes 1. Thermodynamics of the exchange processes

between cadmium ions from solution and sodium ions from zeolite A. *Sep. Sci. Technol.* **1998**, *33*, 449–466.

(13) Mehablia, M. A.; Shallcross, D. C.; Stevens, G. W. Prediction of multicomponent ion exchange equilibria. *Chem. Eng. Sci.* **1994**, *49*, 2277–2286.

(14) Pitzer, K. S.; Peiper, J. C.; Busey, R. H. Thermodynamic properties of aqueous sodium chloride solutions. *J. Phys. Chem. Ref. Data* **1984**, *13*, 1–102.

(15) Pitzer, K. S.; Mayorga, G. J. Thermodynamics of Electrolytes. II Activity and osmotic coefficients for strong electrolytes with one or both ions univalent. *J. Phys. Chem.* **1973**, *77*, 2300–2308.

(16) Kester, D. R.; Pytkowicz, R. M. Sodium, Magnesium and Calcium Sulphate Ion-Pairs in Seawater at 25°C. *Limnol. Oceanogr.* **1969**, *14*, 686–692.

(17) Gaines, G. L.; Thomas, H. C. Adsorption studies on clay minerals. II. A formulation of the thermodynamics of exchange adsorption. *J. Chem. Phys.* **1953**, *21*, 714–718.

(18) Mumford, K. A. *Development of a temperature dependant thermodynamic model for ion exchange*; University of Melbourne: Melbourne, 2008.

(19) Burgess, J. *Metal ions in solution*; Ellis Harwood: Chichester, U.K., 1978.

(20) Richens, D. T. *The chemistry of aqueous ions*; John Wiley & Sons: New York, 1997.

(21) Haung, H. H. Estimation of Pitzer's ion interaction parameters for electrolytes involved in complex formation using a chemical equilibrium model. *J. Solution Chem.* **1989**, *18*, 1069–1084.

(22) Ji, X.; Lu, X.; Zhang, L.; Bao, N.; Wang, Y.; Shi, J. A further study of solid-liquid equilibrium for the NaCl- NH_4Cl-H_2O system. *Chem. Eng. Sci.* **2000**, *55*, 4993–5001.

(23) Clegg, S. L.; Whitfield, M. A chemical model of seawater including dissolved ammonia and the stoichiometric dissociation constant of ammonia in estuarine water and seawater from−2 to 40 degrees C. *Geochim. Cosmochim. Acta.* **1995**, *59*, 2403–2421.

Received for review November 4, 2007. Accepted June 21, 2008. The authors would like to acknowledge funding support provided by the Particulate Fluids Processing Centre, a Special Research Centre of the Australian Research Council, as well as funding support from the Australian Antarctic Science (AAS) grant program (AAS 1300, 2570) through the Australian Antarctic Division.

JE7006428