Adsorption 5, 409–417 (1999)

Competitive Sorption of Copper and Nickel Ions from Aqueous Solution Using Peat

Y.S. HO AND G. MCKAY
Department of Chemical Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, SAR, China

Received May 18, 1998; Revised February 9, 1999; Accepted April 2, 1999

Abstract. Bicomponent aqueous solutions of copper and nickel ions have been used to investigate the sorption of metal ions onto peat. Peat, a low cost sorbent, has shown a high capacity for the sorption of single component metal ions attributed to extensive carboxylic acids within its structure. Copper and nickel ions were selected as typical metals in the effluents of electroplating industries. The effects of competitive sorption in batch systems were studied at various metal ion concentrations. In this study the Butler and Ockrent model was modified using a coefficient, η. Two models were developed based on the interaction coefficient η. The first model incorporates a constant fixed η factor for each metal ion into the Butler-Ockrent equation. The second model incorporates a variable η factor into the Butler-Ockrent equation; this interaction factor varies as a function of sorbent surface coverage. Predicted equilibrium data are found to be in excellent agreement with experimental values using both modified models for various mole ratios of copper and nickel ions in competitive sorption.

Keywords: competitive sorption, copper, nickel, peat, isotherm

Introduction

Peat has been recognised as an effective sorbent for the purification of various industrial wastewaters. It has a significant capacity for many dyes, metal ions, oil, phosphate and others (McKay, 1997) and prepared sphagnum peat moss is less than 10% of the cost of active carbons and molecular sieves. The sorption of heavy metal ions onto sphagnum moss peat from aqueous solution has been studied for single solute systems (Sharma and Forster, 1993; Ho et al., 1994, 1995a). Many studies have been reported concerning the removal of organics from bicomponent organic solution systems (Jain and Snoeyink, 1973; Martin and Al-Bahrani, 1977; Yaacoubi et al., 1991; Fukuchi et al., 1992; Srivastava and Renu, 1995; Suen, 1996), but few have dealt with competitive sorption of metal ions. However, in most cases, industrial wastewaters contain complex mixtures of components. Trujillo et al. (1991) investigated the competitive sorption of six metal ions from wastewater both in batch systems and in semi-continuous packed-bed experiments. The results show that mathematical models can provide effective multi-component equilibrium constants, sorptive capacities and reduced overall mass-transfer coefficients. Gould and Genetelli (1984) have examined the competition between heavy metal ions for binding sites using zinc, nickel, cadmium and copper as test metals. The results show that their sorbent had the highest binding capacity for copper and that this was more or less independent of the others; also copper exerted the largest competing effect. Allen and Brown (1995) have used the Langmuir, the Freundlich and Redlich-Peterson isotherms for multicomponent metal sorption onto lignite. The Triple Layer model (TLM), using surface complexation constants determined from single sorption experiments, successfully predicted cadmium and zinc removal from the two metal solutions (Gabaldón et al., 1996) as well as copper and nickel, copper and cadmium, and copper and zinc removal from the binary systems (Seco et al., 1997). Jain and Snoeyink (1973) found that not only was there sorption with equal competition for sorption sites but also that sorption without competition for different types of site occurred in a binary organic system. In addition, it has been found that the effects of competitive sorption became more marked with the increase in the number of solutes in solution (Martin and Al-Bahrani, 1977).

Shallcross et al. (1988) developed an ion exchange mechanism based on the Law of Mass Action and ionic strengths. Several approaches have been developed and tested to explain ionic strength effects on copper and hydrogen ion titrations in the presence of humic substances. A nonlinear Poisson-Boltzmann equation was used to model the interactions between the charged surfaces of suspended colloids to develop models on ion binding to mineral and organic substances (Dzombak and Morel, 1990). A further development of this model by Bartschat et al. (1992) incorporated additional data on molecular weight distribution, size and functional group content of humic substances and this reduced the number of required fitting parameters. The ion exchange potential of a wide range of biomass systems has been reviewed (Trujillo et al., 1995; Wase and Forster, 1997); these reviews covered sorption onto algae, fungi, bacteria, peat moss, humic substances and cellulosic based substances. The sorption of metal ions onto peat was reported in these reviews as similar to that of a weak polyelectrolyte. Breuer and Melzer (1990a) reported that peat behaved as a relatively ideal ion exchanger and that the heterogeneous nature of peat enhanced sorption. These authors (Breuer and Melzer, 1990b) have determined several equilibrium constants for peat-metal ion systems.

The purpose of this study is to investigate competitive sorption onto peat from aqueous bicomponent mixtures of copper(II) and nickel(II). The two metals are found extensively in effluents from the microelectronics and electroplating industries.

Methods and Materials

Adsorbent

A standard pack (50 dm^3) of sphagnum most peat, supplied by Bord Na Mona-Ireland and commercially available in Britain and Ireland, was used for this work. No form of chemical treatment was applied to the peat. The peat was dried in an oven for 24 h at 105°C, and then screened through a 14 mesh sieve (BS 410/43) to remove any large non peat solids. This procedure produced a uniform material for the experimental studies.

Reagents

Analytical grade reagents were used in all cases. Stock solutions of copper(II) and nickel(II) at 1000 mg/dm^3 were prepared in distilled water using AR copper sulphate and AR nickel sulphate. All working solutions were prepared by diluting the stock solutions with distilled water. The pH adjustments were made using AR sulphuric acid.

Peat Characterisation

The metal content of peat was determined by digesting peat by heating in nitric acid and filtering. The metal ion concentrations were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The concentrations are shown in Table 1.

The batch sorption experiments for single-component systems were carried out on a shaker using capped 125 ml Erlenmeyer conical bottles. In the sorption isotherm tests, 0.5 g of peat was thoroughly mixed with the metal ion solution (125 ml). The concentrations for copper(II) and nickel(II) systems ranged from 0.2 to 3 mmol/dm^3. A similar procedure was used for the bicomponent studies. Three different systems were examined using copper and nickel in the mole ratio of 1 : 1, 1 : 2 and 2 : 1 (Cu : Ni) and the concentration range of 0.1 to 1.6 mmol/dm^3 for both of copper(II) and nickel(II) in the 1 : 1 system, 0.05 to 1 mmol/dm^3 and 1.4 to 2 mmol/dm^3 for copper(II) and nickel(II) in

Table 1. Metal concentrations in original sphagnum peat moss.

Constituent	Concentration (μg/g of peat)	Constituent	Concentration (μg/g of peat)
Iron	890	Cadmium	1.1
Aluminium	660	Potassium	<1
Sodium	285	Chromium	<1
Manganese	24	Copper	<1
Zinc	19	Mercury	<1
Lead	13.5	Silver	<1
Nickel	5.5	Zirconium	<1

Table 2. Final equilibrium pH values at various initial metal ion concentrations.

Initial concentration (C_0 mg/dm^3)	25	50	75	100	150	200	250	300
Final pH value (Cu Systems)	3.60	3.50	3.40	3.30	3.20	3.15	3.10	3.05
Final pH value (Ni Systems)	3.60	3.45	3.40	3.35	3.30	3.25	3.22	3.20

both 1 : 2 and 2 : 1 systems. After shaking the bottles for 3 h, the reaction mixtures were filtered (Whatman No. 1) and the filtrate was analysed for the concentration of copper(II) and nickel(II) using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The sample bottles were shaken in a thermostatically controlled shaking water bath at 25 ± 2°C. The analytical procedures and methods were carried out according to EPA standard methods for metal ion analysis. Previous work (Ho et al., 1994, 1995b) demonstrated that under the experimental conditions used, equilibrium was reached in 2 h. The solution pH values of the initial and final solutions were measured. Initial pH values were 4.50 ± 0.10 and final pH values showed some variation with initial solution concentration. The values are given in Table 2.

The data in Table 2 shows that as the initial metal ion concentration increases, the resultant equilibrium pH decreases. Although after $C_0 = 100$ mg/dm^3 the equilibrium pH values are fairly steady. It can be concluded from this trend that as more metal ions are sorbed onto peat, more hydrogen ions are released from the peat into solution. The hydrogen ion sources are most likely the carboxylic, phenolic and enol groups in the peat. These groups, which are generally considered responsible for the cation exchange capacity of peat, are present in 2–3 milliequivalents/g peat. The intrinsic ionisation potential for the carboxylic acids is about 10^{-5} and therefore it is possible to estimate the ion exchange capacity. The hydrogen ion concentration was increased during the sorption process since there was a pH decrease. This can be calculated for the different initial metal ion concentrations and the differences in pH values from the start of the sorption process until equilibrium is reached.

Table 3 shows the hydrogen ion concentrations at three relevant pH values and two initial metal ion concentrations, $C_0 = 0$ mg/dm^3 and $C_0 = 200$ mg/dm^3 respectively.

Table 3. Hydrogen ion milliequivalent/g peat for different initial pH.

pH$_{\text{in}}$	pH$_0$ (C_0 = 0 mg/1)	Ionisation, H$^+$ (meq/g)	pH$_{200}$ (C_0 = (200 mg/1)	Ion exchange, H$^+$ (meq/g)
3.00	2.92	0.20	2.84	0.24
4.00	3.55	0.18	3.24	0.29
5.00	3.68	0.20	3.29	0.30

Table 4. Specific sorption capacities for various initial pH values for copper and nickel (25°C).

pH$_{\text{in}}$	Monolayer coverage, X_{m} (mg copper/g peat)	Monolayer coverage, X_{m} (mg nickel/g peat)
3.00	12.4	5.53
4.00	15.4	7.84
4.50	15.8	8.13
5.00	16.4	8.52

The influence of pH on the sorption capacity of sphagnum moss peat for copper and nickel is shown in Table 4. The sorption capacities are fairly constant with pH values of 4.0 and 5.0 but as the pH approaches 3 it can be observed that the saturation capacity is beginning to decrease probably due to competition with hydrogen ions at low pH.

Additional experimental details have been reported previously (Ho et al., 1994, 1995a) and this research also indicated the sorption capacities of nickel and copper remained relatively constant with pH over the range 3.5 to 5.0. The final pH values are in the range 3.8 to 4.2 depending on initial metal ion concentration.

Isotherms

Equilibrium sorption studies are performed to provide the capacity of the sorbent. The sorption capacity is described by a sorption isotherm characterised by certain constants whose values express the surface properties and affinity of the sorbent. Sorption equilibrium is established when the concentration of sorbate in the bulk solution is in dynamic balance with that of the interface. Equilibrium relationships between sorbent and sorbate are described by sorption isotherms, usually the ratio between the quantity sorbed and that remaining in the solution at a fixed temperature at equilibrium. The data were determined and analysed in accordance with some of the most frequently used isotherms:

The Langmuir sorption isotherm (Langmuir, 1916) is the best known and most often used isotherm for the sorption of a solute from a liquid solution as:

$$\frac{C_e}{q_e} = \frac{1}{Q_m a_{L,i}} + \frac{C_e}{Q_m} \tag{1}$$

where q_e is the sorption capacity at the equilibrium solute concentration C_e (mmol/g); C_e is the concentration of sorbate in solution (mmol/dm^3); Q_m is the maximum sorption capacity corresponding to complete monolayer coverage (mmol/g); $a_{L,i}$ is a Langmuir constant related to the energy of sorption (dm^3/mmol).

A model for competitive sorption based on the Langmuir equation was first developed by Butler and Ockrent (1930) to describe the sorption equilibrium in multicomponent systems. This isotherm is applicable when each single component obeys Langmuir behaviour in a single-component system. It is widely used to calculate the Langmuir constant Q_m, the amount of solute sorbed per unit weight of sorbent, in the multicomponent systems. The common form for depicting the distribution is to correlate the amount of solute sorbed per unit weight of sorbent with the residual solute concentration remaining in an equilibrium state. If there are two solutes present together in the sorption system the competitive Langmuir isotherms are:

$$q_1 = \frac{Q_{m,1} a_1 C_1}{1 + a_1 C_1 + a_2 C_2} \tag{2}$$

$$q_2 = \frac{Q_{m,2} a_2 C_2}{1 + a_1 C_1 + a_2 C_2} \tag{3}$$

where q_1 and q_2 are the amounts of solutes 1 and 2 sorbed per unit weight of sorbent at equilibrium concentrations C_1 and C_2, respectively. $Q_{m,1}$ and $Q_{m,2}$ are the maximum sorption capacities of solutes 1 and 2, respectively. These are determined from single-component systems and, therefore, correspond to a monolayer coverage of the sorbent. a_1 and a_2 are the Langmuir constants and are a function of the energy of sorption of solutes 1 and 2, respectively. These are also determined from single-component systems.

In this study the Butler and Ockrent model was modified using an interaction coefficient, η, that is a function of sorption capacity. The Butler-Ockrent model was developed to apply the Langmuir isotherm to multicomponent sorption systems. It is effectively an extended Langmuir isotherm.

$$q_1 = \frac{X_1 a_1 \left[\frac{C_1}{\eta_1 (q_i/Q_{m,1})}\right]}{1 + a_1 \left[\frac{C_1}{\eta_1 (q_i/Q_{m,1})}\right] + a_2 \left[\frac{C_2}{\eta_2 (q_i/Q_{m,2})}\right]} \tag{4}$$

$$q_2 = \frac{X_2 a_2 \left[\frac{C_2}{\eta_2 (q_i/Q_{m,2})}\right]}{1 + a_1 \left[\frac{C_1}{\eta_1 (q_i/Q_{m,1})}\right] + a_2 \left[\frac{C_2}{\eta_2 (q_i/Q_{m,2})}\right]} \tag{5}$$

where $\eta_{Cu}(q_i/Q_{m,1})$ and $\eta_{Ni}(q_i/Q_{m,2})$ are the function of interaction coefficients for copper, η_{Cu}, and for nickel, η_{Ni}, and X is the fractional surface coverage.

Results and Discussion

Some of the earliest work on sorption of gases on differently treated surfaces were investigated by Faraday (1834), who first suggested that there must be specific sorption of reactant molecules for surface catalysis. Sorption results from unbalanced forces associated with surface molecules of sorbates or sorbents. The high potential energy of these molecules can be reduced by the attraction of other substances. Sorption therefore presumably occurs exclusively on the surface sites of the sorbent.

The experimental data were analysed by linear regression analysis and a simple Langmuir isotherm was found to provide an excellent description of the sorption with correlation coefficients 0.998 for nickel and 0.999 for copper in the single-component systems. The isotherms given by the Langmuir equation are shown in Fig. 1. It is clear from Fig. 1 that copper has a stronger sorptive potential as its isotherm is located at a lower position in the plot (Srivastava and Tyagi, 1995). The values for the Langmuir constant, Q_m, are 0.198 mmol/g for copper and 0.150 mmol/g for nickel and constants, $a_{L,i}$, are 35.6 dm^3/mmol for copper and 8.50 dm^3/mmol for nickel respectively. It is observed by comparison of the results that copper(II) is removed more extensively than nickel(II) at the same pH and temperature of sorption. The preference of peat for metals has been related to the metal electronegativity of the ions (Allen and Brown, 1995).

The equilibrium capacities prediction of the Butler-Ockrent model was tested by least square regression analysis for the sorption of metal ions onto peat to determine which equation best describe the data. Table 5 shows the agreement between the measured and model

Table 5. Correlation coefficient, r^2, and root mean square error, RMSE, of the equilibrium capacities for binary sorption systems with Butler-Ockrent equation.

Mole ratio Cu(II) : Ni(II)	Copper		Nickel	
	r^2	RMSE	r^2	RMSE
1 : 1	0.997	0.515	0.596	0.0857
1 : 2	0.994	0.665	0.784	3.85
2 : 1	0.991	0.227	0.245	0.973

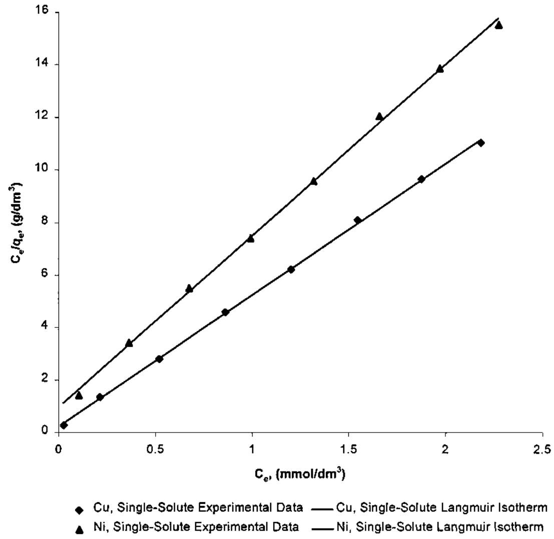

Figure 1. Langmuir isotherms for single-solute system.

predicted data for the binary sorption system. The root mean square error (RMSE) relating the measured and the predicted metal uptakes may be defined for each metal component (Shallcross et al., 1988):

$$E_i = \sum_{i=1}^{n} \left(\frac{q_i - q_i^*}{q_i} \right)^2 \tag{6}$$

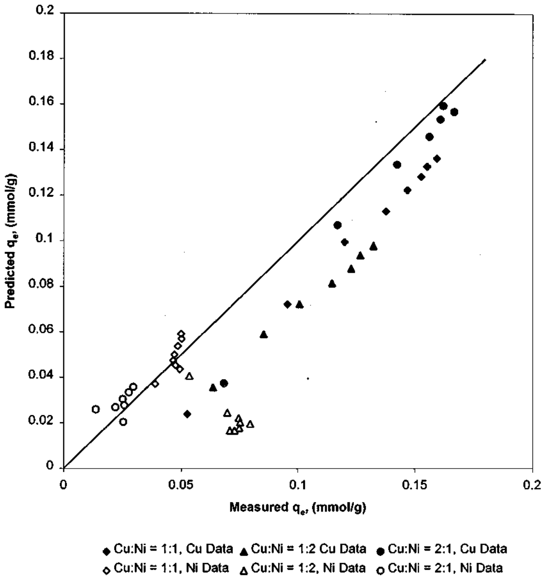

Figure 2. The relationship between measured and predicted equilibrium sorption capacities from Butler-Ockrent equation.

where q_i and q_i^* are the measured and predicted sorption capacities of metal ions onto peat and n is the number of measurements.

Figure 2 shows the relationship between the measured and the model predicted equilibrium sorption capacities of metal ions onto peat for the Butler-Ockrent model. A modified Butler-Ockrent model with an interaction factor η was tested with the data in Table 6 and the plots are shown in Fig. 3. The correlation between the measured and the model predicted data have improved significantly but all the nickel correlation coefficients are less than 0.950. The concept of such an interaction factor was proposed by Schay et al. (1957) and was used with limited success by Mathews and Weber (1978) for the sorption of phenol on carbon and by McKay and Al Duri (1987) for the sorption of basic dyes on carbon. One of the most difficult tasks in

Table 6. Parameters for the relationship between measured and predicted equilibrium sorption capacities for binary sorption systems using the Butler-Ockrent equation modified with constant interaction factor η.

Mole ratio Cu(II) : Ni(II)	Copper			Nickel		
	r^2	η_{Cu}	η_{Ni}	r^2	η_{Cu}	η_{Ni}
1 : 1	0.990	2.91×10^{-3}	9.21×10^{-3}	0.813	1.43×10^{-2}	0.898
1 : 2	0.986	3.67×10^{-3}	1.52×10^{-2}	0.929	1.41×10^{-2}	1.01
2 : 1	0.989	3.16×10^{-3}	6.19×10^{-3}	0.680	3.90×10^{-3}	9.79×10^{-5}

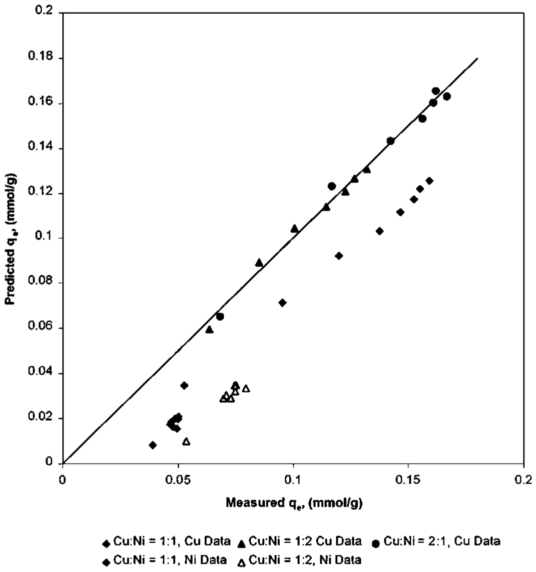

Figure 3. The relationship between measured and predicted equilibrium sorption capacities from modified Butler-Ockrent equation with constant interaction factor.

understanding adsorption phenomena is the quantification of equilibrium isotherms for mixtures. The existing theoretical concepts have been summarised by Ruthven (1984) who identified the usefulness of deriving competitive isotherms exclusively from single component data. The IAS theory, developed for gas phase systems (Myers and Prausnitz, 1965) and extended to dilute solutions (Radke and Prausnitz, 1972) is a thermodynamically sound model using only single component isotherms. The IAS model, based on single component Langmuir equilibrium, was used to test the experimental data in the present paper, but was found to be unsuitable. Competitive isotherms, predicted by the IAS theory reduce to the competitive Langmuir equation if (i) the single component adsorption of each component is a Langmuir isotherm and (ii) the saturation capacities of these Langmuir isotherms are identical. Although the first condition is often satisfied for solutions of simple organics (Huang and Horvath, 1987) the latter is seldom true even for closely related isomers (Golshan-Shirazi et al., 1991; Seidel-Morgenstern, 1993). Further work on organics (Seidel et al., 1986; Seidel and Gebin, 1988) used the Redlich-Peterson and Freundlich isotherm equations in the IAS but still found considerable deviation between results and model predicted data. The authors concluded that chemical interaction in the adsorbed phase could be responsible and that IAS cannot be applied to cases of reaction between adsorbed species. Furthermore, Talu and Myers (1988) stated that the Freundlich and Dubinin-Radushkevich equations are unsuitable for the calculation of spreading pressure. Frances et al. (1995), using different sized molecules, observed that at large surface coverages of larger molecules, for steric and entropic reasons, it is more favourable for small molecules to adsorb and expel larger molecules, this may create a selectivity reversal in the system. On the basis of this recent literature it is not surprising that the application of the IAS model to the present system under investigation does not provide a satisfactory correlation of experimental data. The reasons are summarised:

i) the solutes are ionic species, having different ionic radii;
ii) it is likely that hydrated ionic species may exist in solution, again promoting a degree of selectivity reversal;
iii) the solutes are electrolytes and therefore the system is non-ideal, requiring activity coefficients to better describe the species;
iv) the sorbent, peat, contains a rich myriad of chemicals several of which could react with metal ions by exchange, chelation etc. The surface carboxyl, carbonyl and hydroxyl groups will promote different chemical reactions thus even more complicating the observations by Seidel and Gelbin (1988);
v) the saturation capacities of each metal ion onto peat in single solute systems is different, copper being adsorbed to a greater capacity, which can be attributed in part to the different electronegativities of the two metal ions;
vi) although solute concentrations are relatively low, a twenty-fold range of concentrations has been used and extends well beyond the range of Henry's Law applicability. Equilibrium saturation is also achieved. These two factors indicate the non-ideality of the system.

Based on these six factors, it is apparent that conventional IAS will not apply and that the interaction factor, η, will not remain constant as the sorption process proceeds. The preferential chemical selectivity of the various peat sites will compete for metal ions to varying degrees. The more active sites will attach to the metal ion species first. This, of course, demands an interaction term dependant on the fractional surface coverage, q_i/Q_m.

Table 7. Correlation coefficient, r^2, and root mean square error, RMSE, of the equilibrium capacities for binary sorption systems using the Butler-Ockrent equation modified with an interaction factor η as a function of q_i/Q_m.

Mole ratio Cu(II) : Ni(II)	Copper		Nickel	
	r^2	RMSE	r^2	RMSE
1 : 1	0.999	7.98×10^{-4}	1.000	2.77×10^{-7}
1 : 2	0.998	7.44×10^{-4}	1.000	3.72×10^{-8}
2 : 1	0.995	2.10×10^{-3}	1.000	6.98×10^{-5}

It is apparent from these reasons therefore, that the interaction factor η is not a constant and may be a function of fractional sorbent surface coverage.

As an initial attempt to study this effect single component and multicomponent data have been correlated to obtain $\eta(q_i/Q_m)$.

The Butler-Ockrent model was modified with η as a function of q_i/Q_m as shown in Eqs. (4) and (5). Table 7 shows the extremely high correlation coefficients and low root mean square error demonstrating an excellent fit of the equilibrium capacities from the model predicted values the measured experimental data.

Figure 4 shows the relationship between the measured and the modified model predicted equilibrium sorption capacities of metal ions onto peat. The slope and intercept values of the results of Fig. 4 are shown in Table 8. The slope obtained is 1.000 and the intercept is very low showing an excellent fitting of the equilibrium capacities from the predicted to the measured data.

Table 8. Parameters for the relationship between measured and predicted equilibrium sorption capacities for binary sorption systems using the Butler-Ockrent equation modified with an interaction factor η as a function of q_i/Q_m.

Mole ratio Cu(II) : Ni(II)	Copper		Nickel	
	Slope	Intercept	Slope	Intercept
1 : 1	1.000	0.00×10^{0}	1.000	-6.78×10^{-10}
1 : 2	1.000	2.53×10^{-8}	1.000	-3.11×10^{-8}
2 : 1	1.000	1.10×10^{-3}	1.000	-4.72×10^{-10}

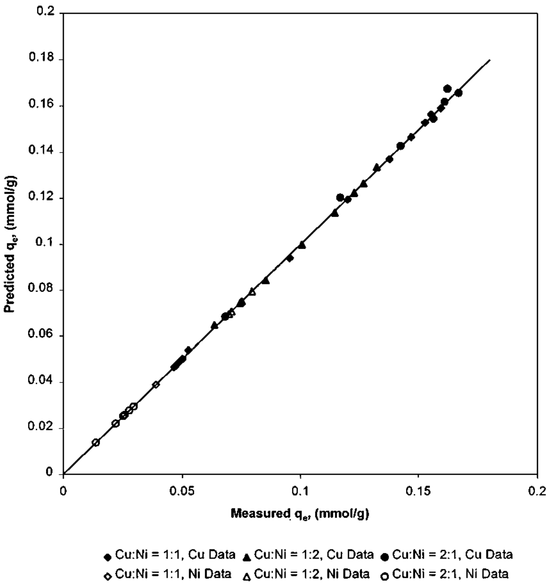

Figure 4. The relationship between measured and predicted equilibrium sorption capacities from modified Butler-Ockrent equation constant interaction factor as a function of q_i/Q_m.

The corresponding linear plots of the values of η against (q_i/Q_m) were regressed to obtain expressions for these values in terms of the (q_i/Q_m) with high correlation coefficients (Table 9). Therefore it is further considered that η can be expressed as a function of (q_i/Q_m) as follows:

$$\eta = \eta_0 \left(\frac{q_i}{Q_m} \right)^{m} \tag{7}$$

The corresponding linear plots of the values of X_{Cu} and X_{Ni} against m were regressed to obtain expressions for these values in terms of the metal ion mole fraction, X, with high correlation coefficients (Table 10). Therefore it is further considered that m can be expressed as a function of X_{Cu} and X_{Ni} as follows:

$$m = A \exp(BX) \tag{8}$$

Figure 5 shows the relationship between the m and X.

The authors have attempted to use various parameters such as electronegativities, ionic radii, activites, relative molar concentrations of metal ions, relative sorption capacities to quantify $\eta(q_i/Q_m)$ in terms of system characteristics. Although the trends show qualitatively dependence on certain of these parameters at present we have not been successful in deriving a quantitative relationship.

Table 9. Empirical parameters for predicted η from (q_i/Q_m) for the modified Butler-Ockrent equation.

		Copper			Nickel		
Cu : Ni		η_0	m	r^2	η_0	m	r^2
1 : 1	Cu	4.13×10^{-2}	2.45	0.999	0.264	3.09	0.997
1 : 2	Cu	2.28×10^{-2}	7.69	0.993	0.103	7.99	0.988
2 : 1	Cu	9.46×10^{-3}	1.04	0.999	2.17×10^{-3}	1.03	1.000
1 : 1	Ni	4.15×10^{13}	31.3	0.997	1.66×10^{11}	23.8	0.999
1 : 2	Ni	7.56×10^{15}	61.2	0.990	1.38×10^{15}	53.7	0.998
2 : 1	Ni	1.14×10^{9}	14.8	0.999	4.14×10^{9}	13.8	0.997

Table 10. Empirical parameters for predicted m from X.

	Copper			Nickel		
	A	B	r^2	A	B	r^2
Copper	56.2	−6.02	0.993	0.140	6.14	0.998
Nickel	253	−4.27	0.999	3.30	4.09	0.988

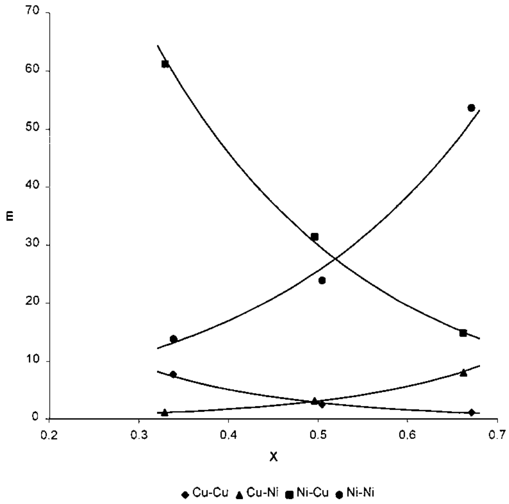

Figure 5. The relationship between the m and X.

Conclusions

Studies on equilibrium sorption in a copper/nickel bicomponent system have shown that competition occurred. An interaction factor which is a function of sorption capacity has been included in the bicomponent competitive sorption model. In this study the Butler and Ockrent model was modified using an interaction coefficient, η. The models were therefore developed as a predictive models for different ratios of metal ion concentrations in competitive sorption and excellent agreement has been obtained between predicted values and experimental data.

References

Allen, S.J. and P.A. Brown, “Isotherm Aanalyses for Single Component and Multi-Component Metal Sorption Onto Lignite,” *Journal of Chemical Technology and Biotechnology*, **62**, 17–24 (1995).

Bartschat, B.M., “Oligoelectrolyte Model for Cation Binding by Humic Substances,” *Environ. Sci. Technol.*, **26**, 284–292 (1992).

Breuer, K. and A. Melzer, “Heavy Metal Accumulation (Lead Cadmium) and Ion Exchange in Three Species of Sphagnacese I. Main Principles of Heavy Metal Accumulation in Sphagnacese,” *Oecologia*, **82**, 461–467 (1990a).

Breuer, K. and A. Melzer, “Heavy Metal Accumulation (Lead and Cadmium) and Ion Exchange in Three Species of Sphagnacese II. Chemical Equilibrium of Ion Exchange and the Selectivity of Single Ions,” *Oecologia*, **82**, 468–475 (1990b).

Butler, J.A.V. and C. Ockrent, “Studies in Electrocapillarity. Part III The Surface Tensions of Solutions Containing Two Surface-Active Solutes,” *Journal of Physical Chemistry*, **34**, 2841–2859 (1930).

Dzombak, D.A. and F.M.M. Morel, *Surface Complexation Modelling*, John Wiley and Sons, New York, 1990.

Faraday, M., “Experimental Researches in Electricity—Sixth Series,” *Philosophical Transactions of the Royal Science of London*, **124**, 55–76 (1834).

Frances, E.I., F.A. Siddiqui, D.J. Ahn, C.H. Chang, and N.H.W. Wang, “Thermodynamically Consistent Equilibrium Adsorption Isotherms for Mixtures of Different-Size Molecules,” *Langmuir*, **11**, 3177–3183 (1995).

Fukuchi, K., S. Kobuchi, and Y. Arai, “Measurement and Prediction of Adsorption Equilibria of Quaternary Organic Solutes from Dilute Aqueous Solutions on Activated Carbon,” *Fundamentals of Adsorption. Proceedings of the Fourth International Conference on Fundamentals of Adsorption*, M. Suzuki (Ed.), pp. 177–184, Elsevier, Amsterdam, London, New York, Tokyo, 1992.

Gabaldón, C., P., Marzal, J. Ferrer, and A. Seco, “Single and Competitive Adsorption of Cd and Zn Onto a Granular Activated Carbon,” *Water Research*, **30**, 3050–3060 (1996).

Golshan-Shirazi, S., J.X. Huang, and G. Guiochon, "Comparison Between an Experimental Isotherm and the Le Van-Vermeulen Model. Application to the Prediction of Band Profiles in a Case of Selectivity Reversal," *Anal. Chem*. **63**, 1147–1153 (1991).

Gould, M.S. and E.J. Genetelli, "Effects of Competition on Heavy Metal Binding by Anaerobically Digested Sludges," *Water Research*, **18**, 123–126 (1984).

Ho, Y.S., D.A.J. Wase, and C.F. Forster, "The Adsorption of Divalent Copper Ions from Aqueous Solution by Sphagnum Moss Peat," *Transactions of the Institution of Chemical Engineers Part B: Process Safety and Environmental Protection*, **17**, 185–194 (1994).

Ho, Y.S., D.A.J. Wase, and C.F. Forster, "Batch Nickel Removal from Aqueous Solution by Sphagnum Moss Peat," *Water Research*, **29**, 1327–1332 (1995a).

Ho, Y.S., D.A.J. Wase, and C.F. Forster, "Peat as a Biosorbent for the Removal of Heavy Metals from Wastewaters," *Challenges and Opportunities in Science and Technology*. W.C. Shih, S.L.L. Chan, and Y.C. Heng (Eds.), The Chinese Institute of Engineers in the U.K., 1995b.

Huang, J.X. and C. Horvath, "Adsorption Isotherms on High Performance Liquid Chromatography Sorbents. I. Peptides and Nucleic Acid Constituents on Octadecyl Silicate," *J. Chromat*., **406**, 275–285 (1987).

Jain, J.S. and V.L. Snoeyink, "Adsorption from Bisolute Systems on Active Carbon," *Water Pollution Control Federation Journal*, **45**, 2463–2479 (1973).

Langmuir, I., "The Constitution and Fundamental Properties of Solids and Liquids," *Journal American Chemical Society*, **38**, 2221–2295 (1916).

Martin, R.J. and K.S. Al-Bahrani, "Adsorption Studies Using Gas-Liquid Chromatography-II. Competitive Adsorption," *Water Research*, **11**, 991–999 (1977).

McKay, G., "Peat for Environmental Applications: A Review," *Dev. Chem. Engng. Mineral Proc*., **4**, 127–156 (1997).

McKay, G. and B. Al-Duri, "Simplified Model for the Equilibrium Adsorption of Dyes from Mixtures Using Activated Carbon," *Chem. Eng. Process*., **22**, 145–146 (1987).

Myers, A.L. and J.M. Prausnitz, "Thermodynamics of Mixed Gas Adsorption," *AIChE J.*, **11**, 121–127 (1965).

Nicolas-Simmonnot, J.O., M.A. Fernandez, P. Cheneviere, M. Bailly, and G. Grevillot, "Model for Capacity Variation of a Weak-Acid and Weak-Base Ion Exchangers as a Function of the Ionic Environment," *Reactive Polymers*, **17**, 39 (1992).

Radke, C.J. and J.M. Prausnitz, "Thermodynamics of Multisolue Adsorption from Dilute Liquid Solutions," *AIChE J*., **18**, 761–768 (1972).

Schay, G.J., F.P. Fejes, and J. Szethmary, "Adsorption of Gases and Gas Mixtures," *Acta Chim Acad Sci Hung*, **12**, 299–308 (1957).

Seco, A., P. Marzal, and C. Gabaldón, "Adsorption of Heavy Metals from Aqueous Solutions onto Activated Carbon in Single Cu and Ni Systems and in Binary Cu-Ni, Cu-Cd and Cu-Zn Systems," *Journal of Chemical Technology and Biotechnology*, **68**, 23–30 (1997).

Seidel, A. and D. Gelbin, "On Applying the Ideal Adsorbed Solution Theory to Multicomponent Adsorption Equilibria of Dissolved Organic Component on Activated Carbon," *Chem. Engng. Sci*., **41**, 79–89 (1988).

Seidel, A., G. Reschke, S. Friedrich, and D. Gelbin, "Equilibrium Adsorption of Two-Component Organic Solutes from Aqueous Solutions Onto Activated Carbon," *Ads. Sci. Technol*, **3**, 189–199 (1986).

Seidel-Morgenstern, A. and G. Guiochon, "Modelling of Competitive Isotherms and the Chromatographic Separation of Two Enantiomers," *Chem. Eng. Sci*., **48**, 2787–2797 (1993).

Shallcross, D.C., C.C. Herrmann, and B.J. McCoy, "An Improved Model for the Prediction of Multicomponent Ion Exchange Equilibria," *Chemical Engineering Science*, **43**, 279–288 (1988).

Sharma, D.C. and C.F. Forster, "Removal of Hexavalent Chromium Using Sphagnum Moss Peat," *Water Research*, **27**, 1201–1208 (1993).

Srivastava, S.K. and R. Tyagi, "Competitive Adsorption of Substituted Phenols by Activated Carbon Developed from the Fertilizer Waste Slurry," *Water Research*, **29**, 483–488 (1995).

Suen, S.Y., "A Comparison of Isotherm and Kinetic Models for Binary-Solute Adsorption to Affinity Membranes," *Journal of Chemical Technology and Biotechnology*, **65**, 249–257 (1996).

Talu, O. and A.L. Myers, "Rigorous Thermodynamic Treatment of Gas Adsorption," *AIChE J.*, **34**, 1887–1893 (1988).

Trujillo, E.M., T.H. Jeffers, C. Ferguson, and Q. Stevenson, "Mathematically Modeling the Removal of Heavy Metals from a Wastewater Using Immobilized Biomass," *Environmental Science and Technology*, **25**, 1559–1564 (1991).

Trujillo, E.M., M. Spinti, and H. Zhuang, "Immobilized Biomass: A New Class of Heavy-Metal Selective Ion Exchangers," "*Ion Exchange Technology: Advances in Pollution Control*," A.K. Sengupta (Ed.), chap. 6, pp. 225–270, Technomic Publishing Co., 1995.

Wase, J. and C. Forster, *Biosorbents for Metal Ions*. chap. 1, pp. 1–9, Taylor and Francis, U.K., 1997.

Weber, W.J. Jr., and A.P. Mathews, "Effects of External Mass Transfer and Intraparticle Diffusion on Adsorption Rates in Slurry Reactors," *AAAIChE Symp. Ser. Water*, **73**, 91–98 (1976).

Yaacoubi, A., M. Mazet, and O. Dusart, "Competitive Effect in Bi-Solute Adsorption Onto Activated Carbon: DSS, Alcohols and Phenols as Solutes," *Water Research*, **25**, 929–937 (1991).