Correlative biosorption equilibria model for a binary batch system

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Abstract

The binary sorption of copper and nickel ions onto peat has been studied. Equilibrium isotherms have been determined for three different copper : nickel molar concentration ratios. The experimental results have been analysed using an extended multicomponent Langmuir equation with a competition term but the correlation between the experimental and the predicted values was poor. An interaction factor was incorporated into the extended Langmuir equation and a significant improvement in correlation was obtained. The final model involved deriving an expression to correlate the interaction factor with surface loading and these correlations produced coefficients greater than 0.995 for all the isotherms. An F-test on the variable interaction factor model developed in this paper confirmed that it produces a significant improvement in correlating isotherm equilibria data. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Competition sorption; Copper; Nickel; Peat; Isotherm

1. Introduction

The sorption of heavy metal ions onto biosorbents from aqueous solution has been studied for single solute systems (Gosset, Trancart & Thevenot, 1986; Allen, Brown, Mckay & Flynn, 1992; Ho, Wase & Forster, 1995; Xie, Chang & Kilbane, 1996). The influence of a second metal has also been investigated (Gould & Genetelli, 1984; Trujillo, Jeffers, Ferguson & Stevenson, 1991; Niu, Xu, Wang & Volesky, 1993). Chong and Volesky (1996) reported a description of a two metal biosorption equilibrium using Langmuir-type models. There have been several extended Langmuir models applied to multicomponent sorption systems. Butler and Ockrent (1930) and Markham and Benton (1931) reported a modified model on the basis of kinetic considerations alone. Jain and Snoeyink (1973) developed an extended Langmuir model by adding a term based on the hypothesis that in a multicomponent system adsorption occurs both with and without competition. A two-term expansion of the isotherm for competition equilibrium of the two components of a binary mixture has also been reported (Levan & Vermeulen, 1981). Recently, McKay and Porter (1997) reported modified models for predicting muticomponent equilibrium sorption isotherms on the basis of interaction factor considerations. However, few have dealt with detailed predictive models for the sorption of metal ions in a binary system, largely because of the extensive experimental investigations required to obtain test data. The present paper investigates the binary sorption of copper and nickel ions onto peat using three molar ratios of Cu : Ni. A model has been developed by incorporating an interaction factor correlation into the multicomponent Langmuir equation.

2. Methods and materials

The batch sorption experiments for single-component systems were carried out using a constant-temperature shaking water bath and a series of capped 125 ml conical flasks. In the sorption isotherm tests, 0.5 g of peat was thoroughly mixed with the metal ion solution (125 ml). The concentrations of the two metal, copper and nickel, ion systems ranged from 0.2 to 3 mmol/dm³. A similar procedure was used for the bi-component studies. Three different systems were examined using copper and nickel in the molar ratio of 1 : 0.983, 1 : 1.96 and 2.04 : 1 (Cu : Ni) and in the concentration range of 0.1–1.6 mmol/dm³ for both of copper and nickel ions in the 1 : 0.983 system, 0.05–1 and 1.4–2 mmol/dm³ for copper and nickel ions in 1 : 1.96 and 2.04 : 1 systems. After

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shaking the bottles for 3 h, the reaction mixtures were filtered (Whatman No. 1) and the filtrate was analysed for the concentration of copper and nickel ions using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

3. Isotherms

Equilibrium sorption studies provide the capacity of the sorbent, which can be 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. 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 the most often used isotherm for the sorption of a solute from a liquid solution:

$$\frac{C_e}{q_e} = \frac{1}{Q_m a_L} + \frac{C_e}{Q_m}, \tag{1}$$

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 is a Langmuir constant related to the energy of sorption (dm^3/mmol).

Butler and Ockrent (1930) developed a model for competitive sorption based on the Langmuir equation. 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 sorbate 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 extended 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. These Langmuir equations are simple extensions of the single-component Langmuir isotherms to account for multicomponent sorption. They assume that each component adsorbs onto the surface according to ideal solute behaviour under homogeneous conditions with no interaction or competition between molecules taking place.

Jain and Snoeyink (1973) investigated competitive sorption on activated carbon from aqueous bi-component solutions of organic sorbates and developed a model that predicts sorption equilibria in such non-ideal systems. According to Jain and Snoeyink, the Langmuir theory for binary sorbate systems is based on sorption without competition. Therefore, in order to account for competition in the Langmuir theory, the Jain–Snoeyink (JS) model proposed to add an additional term into Eq. (2).

$$q_1 = \frac{(Q_{m,1} - Q_{m,2}) a_1 C_1}{1 + a_1 C_1} + \frac{Q_{m,2} a_1 C_1}{1 + a_1 C_1 + a_2 C_2}. \tag{4}$$

The additional term of Eq. (4) is the Langmuir expression for the number of molecules of solute 1 that sorb without competition on the surface area and the term is proportional to $(Q_{m,1} - Q_{m,2})$. The second term on the right-hand side of Eq. (4), represents the number of molecules of solute 1 sorbed on the surface area proportional to $Q_{m,2}$ in competition with solute 2, and is based on the Langmuir model for competitive sorption. The number of molecules of solute 2 sorbed on the sorbent surface is proportional to $Q_{m,2}$ in competition with solute 1, can be calculated from Eq. (3).

In the present paper, the Jain and Snoeyink model has been modified using an interaction coefficient, η, that is a function of sorption capacity:

$$q_1 = \frac{(X_1 - X_2) a_1 \left[\dfrac{C_1}{\eta_1 \left(\dfrac{q_i}{Q_{m,1}} \right)} \right]}{1 + a_1 \left[\dfrac{C_1}{\eta_1 \left(\dfrac{q_i}{Q_{m,1}} \right)} \right]} + \frac{X_1 a_1 \left[\dfrac{C_1}{\eta_1 \left(\dfrac{q_i}{Q_{m,1}} \right)} \right]}{1 + a_1 \left[\dfrac{C_1}{\eta_1 \left(\dfrac{q_i}{Q_{m,1}} \right)} \right] + a_2 \left[\dfrac{C_2}{\eta_2 \left(\dfrac{q_i}{Q_{m,2}} \right)} \right]}, \tag{5}$$

$$q_2 = \cfrac{X_2 a_2 \left[\cfrac{C_2}{\eta_2 \left(\cfrac{q_i}{Q_{m,2}} \right)} \right]}{1 + a_1 \left[\cfrac{C_1}{\eta_1 \left(\cfrac{q_i}{Q_{m,1}} \right)} \right] + a_2 \left[\cfrac{C_2}{\eta_2 \left(\cfrac{q_i}{Q_{m,2}} \right)} \right]}, \qquad (6)$$

where $\eta_{Cu}(qi/Q_{m,1})$ and $\eta_{Ni}(q_i/Q_{m,2})$ are the interaction coefficients.

4. Results and discussion

Sorption is the concentration of a solute molecule at the surface of a sorbent. Some of the earliest work on the sorption of gases on differently treated surfaces has been 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 data were examined 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 property as its isotherm is located at a lower position in the plot (Srivastava & Tyagi, 1995). The values for the Langmuir constant, Q_m, were 0.198 mmol/g for copper and 0.150 mmol/g for nickel and constant, a_L, were 35.6 dm^3/mmol for copper and 8.50 dm^3/mmol for nickel. It is observed by comparison of the results that copper ion is removed more extensively than nickel ion at the same pH and temperature of sorption.

The equilibrium capacities predicted by the original JS isotherm equation were analysed by the least-square regression analysis for the sorption of metal ions onto peat to determine the quality of fit of the most suitable equation describing the data. Table 1 shows the agreement between the measured and model-predicted data for the binary sorption systems at the
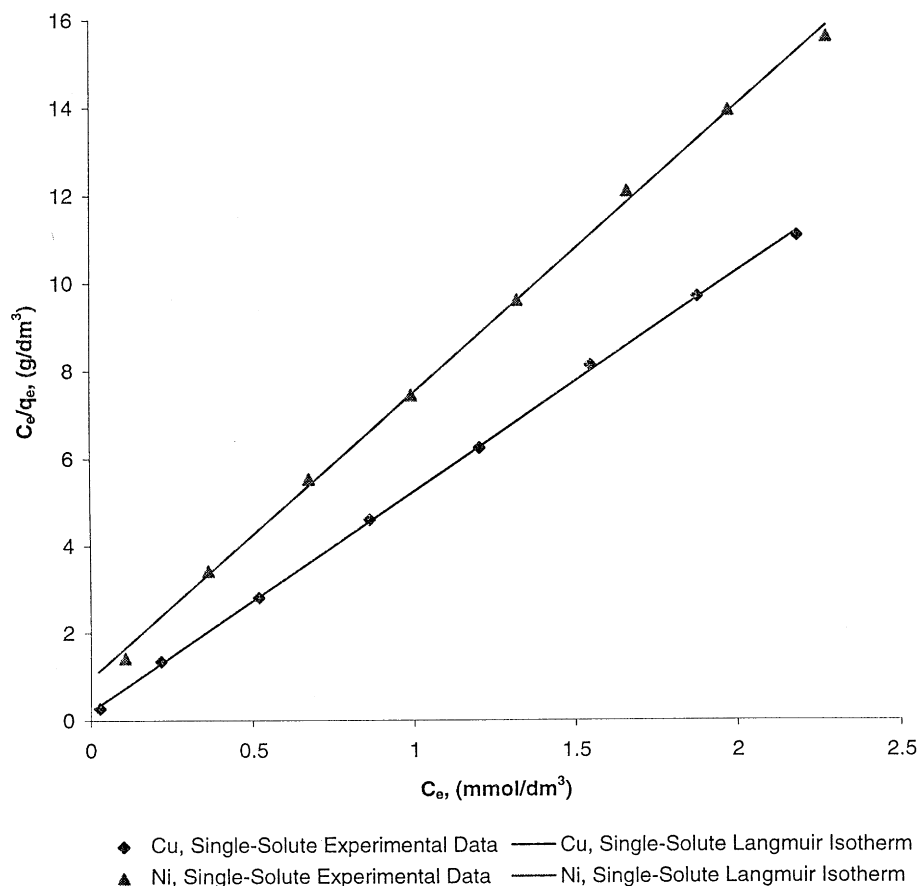

Fig. 1. Langmuir isotherms for single-solute system.

Table 1
Correlation coefficient, r^2, and root mean square error, RMSE, of the equilibrium capacities for binary sorption systems with Jain-Snoeyink equation

Mole ratio	Copper		Nickel	
Cu(II) : Ni(II)	r^2	RMSE	r^2	RMSE
1 : 0.983	0.992	0.309	0.596	0.0857
1 : 1.96	0.985	0.149	0.784	3.85
2.04 : 1	0.988	0.190	0.533	0.402

three metal ion concentration ratios. The root mean square error (RMSE) relating the measured and the predicted metal uptakes may be defined for each metal component (Shallcross, Herrmann & McCoy, 1988):

$$E_i = \sum_{i=1}^{n} \left(\frac{q_i - q_i^*}{q_i} \right)^2, \tag{7}$$

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

Fig. 2 shows the relationship between the measured and the model-predicted equilibrium sorption capacities of metal ions onto peat for the JS model.

A modified JS model with a constant coefficient η was tested with the data in Table 2 and is shown in Fig. 3. A range of interaction factor values for the copper system, η_{Cu}, and the nickel, η_{Ni}, were selected and substituted into Eqs. (5) and (6). The two specific values of each interaction factor, which provide the minimum residual defined by Eq. (7), are then selected as the model values for η_{Cu} and η_{Ni}. The correlation between the measured values and the model-predicted data appear to have improved significantly over the data in Fig. 3 predicted by the original JS model. However, several of the data points, at lower uptake values, still deviate considerably from the regression line. It is apparent that the interaction coefficient η is not a constant and could be a function of solution concentration. An F-test is carried out later in the paper to fully assess if this model, using constant η,
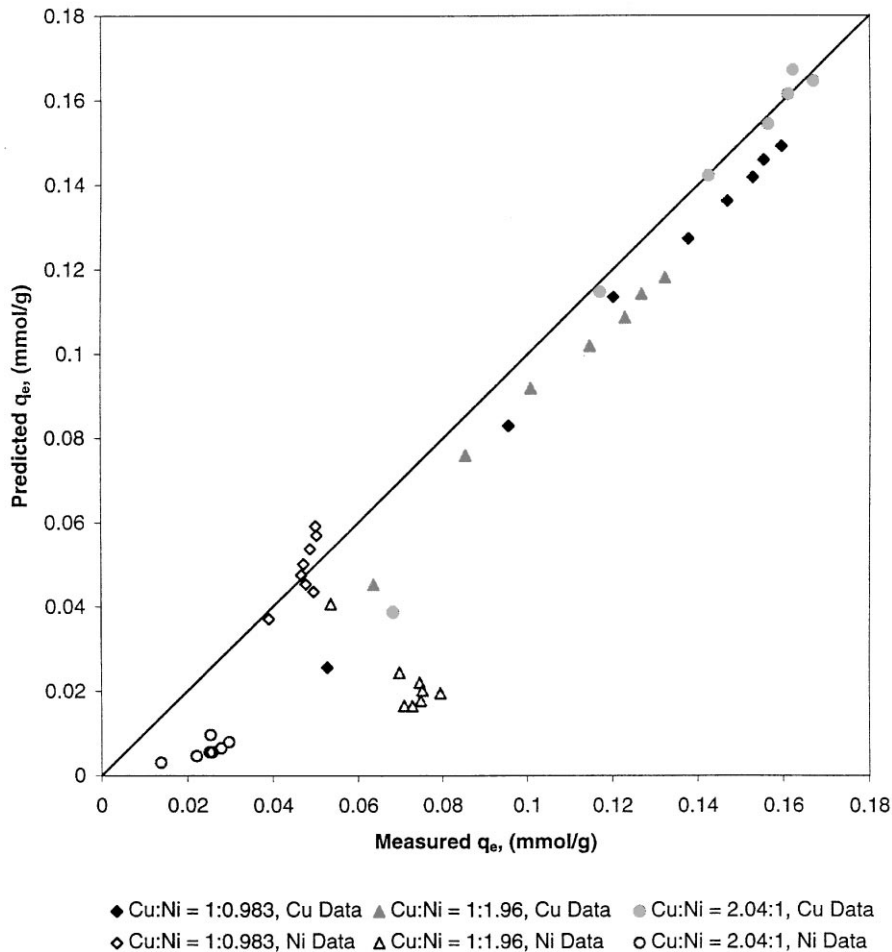

Fig. 2. The relationship between measured and predicted equilibrium sorption capacities from JS equation.
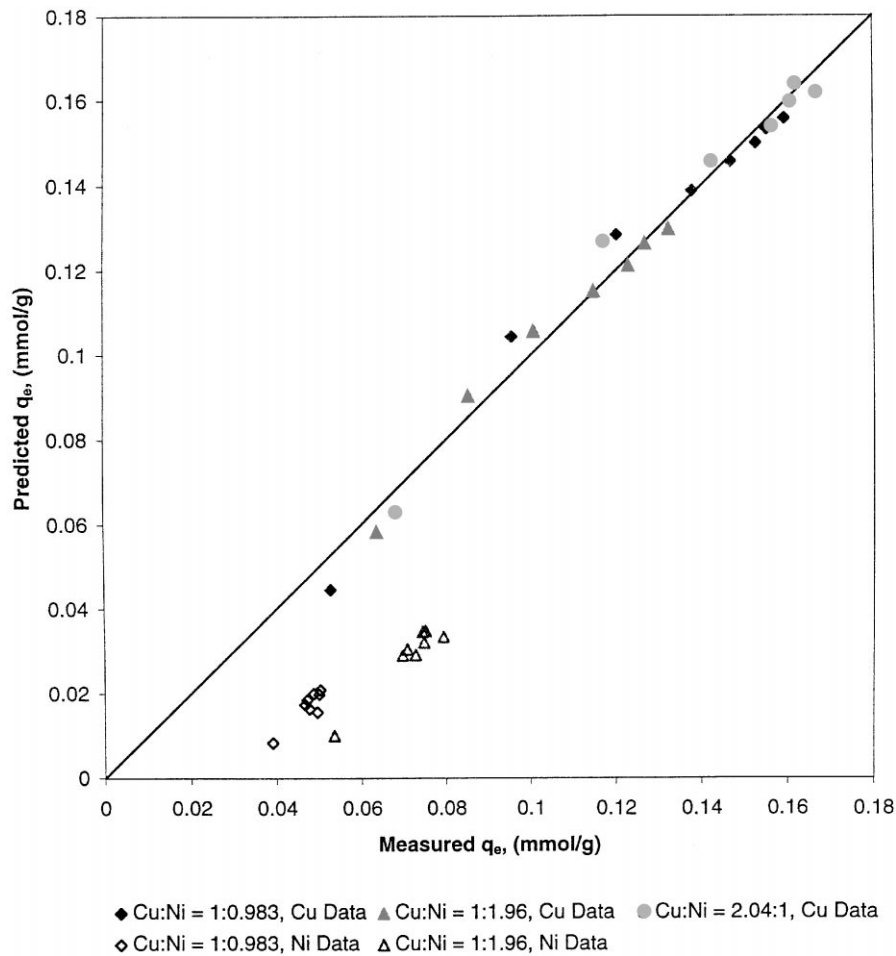
Fig. 3. The relationship between measured and predicted equilibrium sorption capacities from modified JS equation with constant interaction factor.

Table 2
Parameters of the relationship between the measured and the predicted equilibrium sorption capacities for binary sorption systems using JS equations modified with constant interaction factor η

Mole ratio	Copper			Nickel		
Cu(II) : Ni(II)	r^2	η_{Cu}	η_{Ni}	r^2	η_{Cu}	η_{Ni}
1 : 0.983	0.975	0.422	0.475	0.813	1.43×10^{-2}	0.898
1 : 1.96	0.977	0.646	0.842	0.929	1.41×10^{-2}	1.01
2.04 : 1	0.978	0.414	0.314	0.680	3.90×10^{-3}	9.79×10^{-5}

represents a significant improvement to the JS model or not.

The effect of the second metal is a function of, for example, the temperature, the initial metal ion concentration, the dose and the nature of solute–sorbent interaction (Seco, Marzal, Gabaldón & Ferrer, 1997). The preference of several hydrous solids for metals has been related to the metal electronegativity of the ions (Allen & Brown, 1995) or the equilibrium constant of the first metal hydrolysis reaction (Corapcioglu & Huang, 1987).

The modified JS model was now adapted further by using a correlative expression for η as a function of q_i/Q_m (Eqs. (5) and (6)). Table 3 shows the extremely high correlation coefficients and low root mean square error indicating an excellent fitting of the equilibrium capacities from the model-predicted data to the experimentally measured values.

Fig. 4 shows the relationship between the measured and the modified model-predicted equilibrium sorption capacities of metal ions onto peat. The slope and intercept

Table 3
Correlation coefficient, r^2, and root mean square error, RMSE, of the equilibrium capacities for binary sorption systems using JS equation modified with an interaction factor η as a Function of q_i/Q_m

Mole ratio	Copper		Nickel	
Cu(II) : Ni(II)	r^2	RMSE	r^2	RMSE
1 : 0.983	1.000	2.16×10^{-4}	1.000	2.77×10^{-7}
1 : 1.96	1.000	1.50×10^{-4}	1.000	3.72×10^{-8}
2.04 : 1	0.999	3.01×10^{-4}	1.000	6.98×10^{-5}

Table 4
Parameters of the relationship between the measured and the predicted equilibrium sorption capacities for binary sorption systems using JS equation modified with an interaction factor η as a function of q_i/Q_m

Mole ratio	Copper		Nickel	
Cu(II) : Ni(II)	Slope	Intercept	Slope	Intercept
1 : 0.983	1.000	5.33×10^{-12}	1.000	-6.78×10^{-10}
1 : 1.96	1.000	2.64×10^{-7}	1.000	-3.11×10^{-8}
2.04 : 1	0.999	-4.67×10^{-7}	1.000	-4.72×10^{-10}

values of the results shown in Fig. 4 are presented in Table 4. The slopes obtained are 1.000 and intercepts are very low showing an excellent fitting of the equilibrium capacities from the predicted to the measured data.

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 correla-

tion coefficients (Table 5). Therefore it is further considered that η can be expressed as a function of (q_i/Q_m) as follows:

$$\eta = \eta_0 \left(\frac{q_i}{Q_m} \right)^m. \tag{8}$$

The values of m for copper are in the range 1–10 and those for nickel in the range 10–100 varying with initial
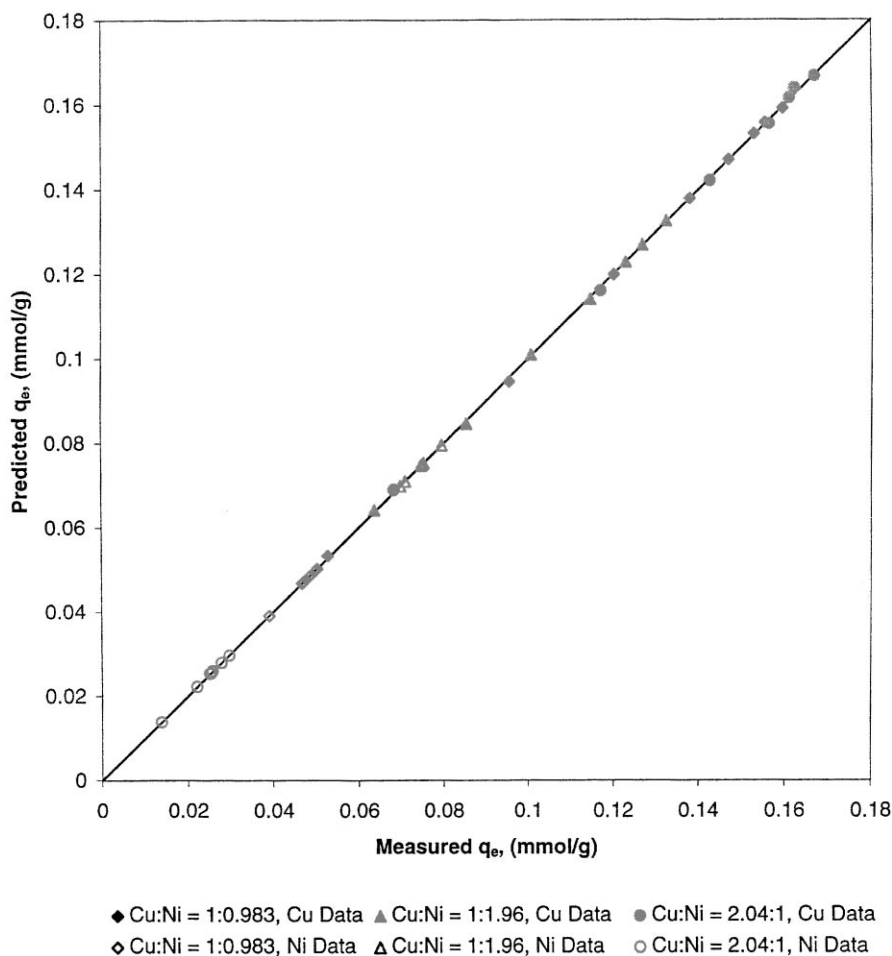

Fig. 4. The relationship between measured and predicted equilibrium sorption capacities from modified JS equation with an interaction factor as a function of q_i/Q_m.

Table 5
Empirical parameters for predicted η from (q_i/Q_m) for modified JS equation

Cu : Ni		Copper			Nickel		
		η_0	m	r^2	η_0	m	r^2
1 : 0.983	Cu	9.99×10^{-2}	2.87	0.999	0.201	5.03	0.999
1 : 1.96	Cu	0.588	5.45	0.999	1.41	7.01	0.999
2.04 : 1	Cu	2.25×10^{-4}	1.51	0.999	2.51×10^{-4}	3.58	0.999
1 : 0.983	Ni	4.15×10^{13}	31.3	0.997	1.66×10^{11}	23.8	0.999
1 : 1.96	Ni	7.56×10^{15}	61.2	0.990	1.38×10^{15}	53.7	0.998
2.04 : 1	Ni	1.14×10^{9}	14.8	0.999	4.14×10^{9}	13.8	0.997

Table 6
Empirical parameters for predicted m from X

	Copper			Nickel		
	A	B	r^2	A	B	r^2
Copper	20.0	-3.85	1.000	1.84	2.02	1.000
Nickel	253	-4.27	0.999	3.30	4.09	0.988

metal ion concentration ratios. This variation of m with metal ion type and concentration ratio suggests that certain inherent properties of the specific metal ion and the metal ion–metal ion interactions are involved in the value of m. Consideration by the present authors has been given to metal ion diameter, electronegativity, and ionisation potential in m. However, no fundamental correlation has been established to date.
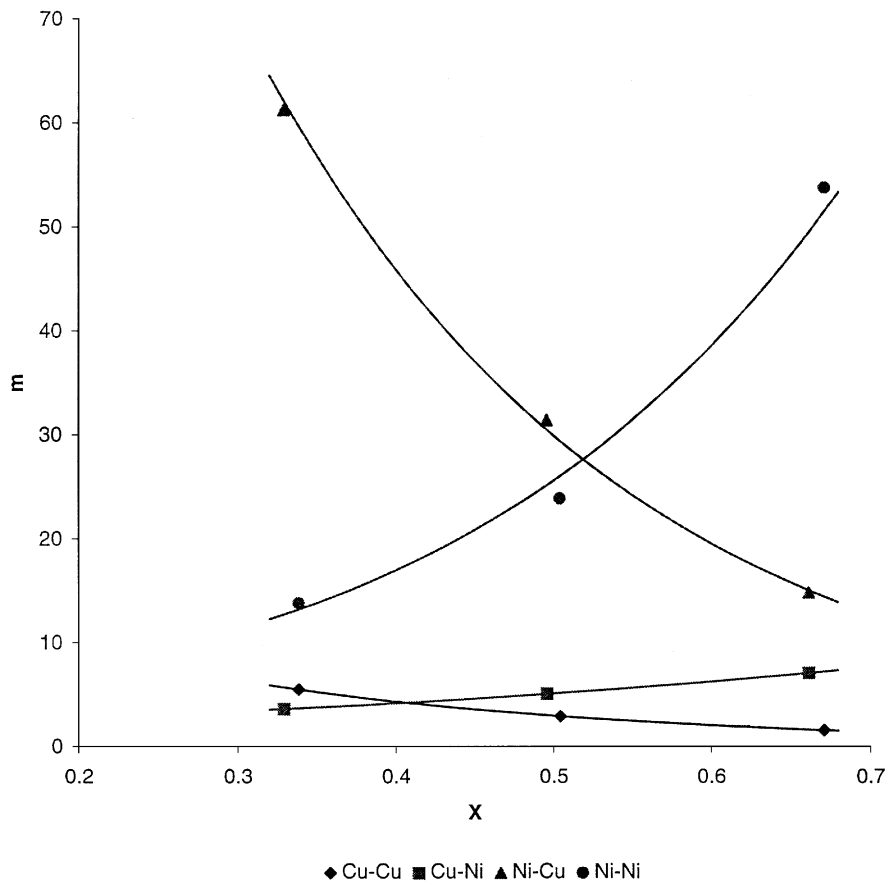

Fig. 5. The relationship between m and X.

Table 7
F-Test at the 95% probability level

Model	Mol ratio	Metal ion	Standard deviation	*F*-test value		Degrees of freedom	Critical *F*-factor
JS(A)	1.000	Cu	6.22×10^{-3}			7 : 7	3.86
	0.983	Ni	2.88×10^{-3}			7 : 7	3.86
JS(B)				A/B			
Constant	1.000	Cu	3.36×10^{-3}	4.83		7 : 6	4.19
eta	0.983	Ni	1.73×10^{-3}	2.68		7 : 6	4.19
JS(C)				A/C	B/C		
Correlative	1.000	Cu	2.68×10^{-4}	539	157	7 : 5	4.28
eta	0.983	Ni	4.45×10^{-6}	1.95×10^{6}	1.51×10^{5}	7 : 5	4.28
JS(A)	2.040	Cu	3.25×10^{-3}			7 : 7	3.86
	1.000	Ni	4.62×10^{-3}			7 : 7	3.86
JS(B)				A/B			
Constant	2.040	Cu	2.17×10^{-3}	2.24		7 : 6	4.19
eta	1.000	Ni	2.06×10^{-3}	5.02		7 : 6	4.19
JS(C)				A/C	B/C		
Correlative	2.040	Cu	2.31×10^{-4}	198	88.2	7 : 5	4.28
eta	1.000	Ni	2.54×10^{-6}	6.582×10^{5}	7.92×10^{5}	7 : 5	4.28
JS(A)	1.000	Cu	1.06×10^{-2}			7 : 7	3.86
	1.960	Ni	3.88×10^{-3}			7 : 7	3.86
JS(B)				A/B			
Constant	1.000	Cu	2.95×10^{-3}	12.9		7 : 6	4.19
eta	1.960	Ni	5.11×10^{-3}	0.58		7 : 6	4.19
JS(C)				A/C	B/C		
Correlative	1.000	Cu	4.29×10^{-4}	611	47.4	7 : 5	4.28
eta	1.960	Ni	3.58×10^{-5}	1.18×10^{4}	2.04×10^{4}	7 : 5	4.28

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 6). Therefore, it is further considered that m can be expressed as a function of X_{Cu} and X_{Ni} as follows:

$$m = A \exp(BX) \qquad (9)$$

Fig. 5 shows the relationship between m and X.

4.1. Statistical comparison of models

The most effective way of comparing the improvements in the two correlative models with the original JS model is by using an *F*-test. The standard deviations of the three multicomponent models, namely, Jain–Snoeyink (JS), Jain–Snoeyink with constant eta (JSCN) and Jain–Snoeyink with variable eta (JCVN) using Eq. (7) have been determined relative to the experimental data. The standard deviations, s^2, for the three models at the three different metal ion mole ratios are shown in Table 7.

The improvement in the various models can now be assessed by means of an *F*-test, for example

$$F = \frac{s_A^2}{s_B^2}. \qquad (10)$$

The standard deviation of the data expected to produce the better fit or significant improvement are placed on the denominator. Column 5 in Table 7 shows the *F*-test values based on various comparisons of the models.

The constant eta (JSCN) model and the variable eta (JSVN) are compared with the original JS model as shown by the values under A/B (JS : JSCN) and A/C (JS : JSVN). In addition, the *F*-test has been performed to assess if there is any significant improvement in using the variable eta model, based on Eq. (7) relative to the constant eta model. These *F*-test values are also shown in column 5 as B/C (JSCN : JSVN). The significance of improvement in any of the models is evaluated by comparing the *F*-test values with standard *F*-test critical values at various probability levels based on the degrees of freedom of the system for the numerator and the denominator. The critical values at the 5% probability level and the degrees of freedom for each system are

presented in Table 7. The F-test may be used to provide insights into either of the two newly developed equations, firstly, whether method A is more precise than method B, and secondly, whether there is a difference in the precision of the two methods. In terms of the first criterion, a comparison of the F-test values in Table 7, indicates that in five results out of the six the JSCN model provides a better fit than the JS model to the experimental data. In the case of the variable eta model, JSVN, when compared to the JS model, it provides a better fit to the experimental data in all six cases, and similarly, by comparing the JSVN data with the constant eta model, JSCN, the JSVN model data were better.

In terms of the second criteria, based on comparing F-values at the 5% probability level for the JS and JSCN models, three out of six sets of F-values fail to confirm that the JSCN model does correlate the experimental data better than the original JS model. In the case of the variable eta model, this model does have significantly greater precision at the 95% probability level than the JS and JSCN models. The model is a significant improvement on previously reported models.

5. Conclusions

A series of modified extended multicomponent Langmuir isotherms have been used to correlate binary copper–nickel equilibrium sorption study results using peat as an adsorbent. Three Cu : Ni molar ratios were used. A correlative expression for the interaction factor and surface loading has been developed and enables the experimental sorption values to be correlated with model data point with coefficients greater than 0.995. The significance of two new models was assessed using an F-test. The first model, using a constant interaction factor η, was shown not to be a significant improvement at the 95% probability level. However, the second model, using a variable correlative interaction factor expression, made a very significant improvement.

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