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Modeling Batch Equilibrium and Kinetics of Copper Removal by Crab Shell

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ABSTRACT

The adsorption characteristics of copper from aqueous solutions on crab shell were determined by batch tests. The uptake equilibrium and kinetics were affected by the pH of the sorption system. In the pH range of 3 to 6, the extent of copper removal was found to increase with increasing pH. A Langmuir–Freundlich model with pH-dependent parameters and an extended Langmuir–Freundlich model with pH-independent parameters were found to account very well for the measured constant pH equilibrium isotherms. Four existing rate models (second-order reversible reaction, second-order irreversible reaction, pseudofirst-order, and Elovich) were evaluated in simulating transient sorption profiles measured over a pH range of 3 to 6. The rate coefficients of the

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four models exhibited a linear dependence on the pH of the sorption system. Given the mathematical simplicity of the four rate models and their apparent success in accounting for the experimental observations throughout the whole time course of sorption, any one of the models can be used as a means for predicting the transient behavior of the copper–crab shell sorption system with reasonable accuracy.

Key Words: Adsorption; Chitosan; Crab shell; Equilibrium; Kinetics; Modeling.

INTRODUCTION

Process waste streams from mining operations, metal plating, and electronic device manufacturing operations often contain heavy metal ions. Improper treatment of these waste streams may lead to the discharge of metals to the environment, causing serious pollution problems. Since heavy metal ions are extremely toxic to plant and animal life and cannot be degraded biologically into harmless products, they must be removed from the contaminated water in order to meet increasingly stringent environmental quality standards. Among the various methods available for metal removal from aqueous solutions, adsorption has been recognized as one of the more effective treatment processes, especially for the pretreatment or polishing of industrial waste streams containing metal ions in trace quantities. Activated carbon has long been recognized as an effective metal removal sorbent. However, the relatively high cost of activated carbon has led to a search of low-cost sorbent materials as potential replacement for the effective but expensive activated carbon, as documented in a recent review.[1] The efficiency of metal removal by these sorbents varies from one material to another.

Among the various novel sorbents, crustacean shells, a by-product of the shellfish processing industry, exhibit promising surface binding specificity toward a range of toxic metal ions.[2–5] The processing wastes of aquatic species such as shrimps, prawns, crabs, and clams contain ~10 to 55% of chitin on a dry weight basis, depending on the method of processing. Chitin, a homopolymer comprising β-(1-4)-*N*-acetyl-D-glucosamine, and its deacetylated derivative, chitosan, are responsible for the sorption of metal ions from aqueous solution. The versatility of chitosan as a metal removal sorbent is mainly due to its highly reactive amino groups ($-NH_2$) at the C-2 position that can serve as coordination sites for many metals. Chitosan is prepared from chitin by deacetylation with a strong alkaline solution. Commercial production of chitosan from the shells of crabs and shrimps in Japan accounts for ~90% of the global chitosan market.[6] It is a highly versatile molecule with commercial applications in a wide range of areas ranging from waste management and medicine to food processing and personal-care products.

Numerous studies have demonstrated the effectiveness of chitosan and derived products in the uptake of metal cations such as lead, cadmium, copper, zinc, and nickel,[7–11] oxyanions,[12] as well as complexed metal ions.[13–16] Information on sorption kinetics and equilibrium is needed for sorbent evaluation and/or process design and optimization. In general, such information cannot be predicted from first principles and is usually obtained from experimental studies as the extent of sorption depends on several factors such as the source of chitosan, the degree of deacetylation, the nature of the metal ion, and solution conditions such as pH. The resulting data can be used to develop and test mathematical models that provide a quantitative means of capturing the sorption characteristics under various conditions. Recently, several relatively simple mathematical models of the kinetics of metal sorption in batch adsorbers have been proposed. These models, ranging from totally empirical ones,[17,18] to semi-empirical types, such as the pseudofirst-order reaction, second-order reaction, and Elovich equations,[19–23] have been compared with experimental data. In many of the semi-empirical approaches, the sorption process is defined in terms of a chemical reaction and the problems of quantifying intrinsic sorption kinetics as well as mass-transfer resistance effects have been circumvented by using empirically determined ''lumped'' parameters. Although these rate models are simpler in computational terms and can be a useful aid to process design and optimization, they clearly have significant limitations. In many instances, the predictive power of these models depends on empirical correlation of their rate parameters with system variables such as the initial adsorbate concentration and mass of sorbent.[21,22] Although it is well known that for many sorption systems, metal uptake is often controlled by solution pH, very few studies have examined the ability of these models to predict the effect of pH on sorption kinetics.

The present work examined the ability of four existing rate models (second-order reversible reaction, second-order irreversible reaction, pseudo-first order, and Elovich) for quantifying and predicting the sorption behavior of copper on crab shell as a function of solution pH in a more systematic way than in previous studies. A number of studies investigated the predictive capability of these rate models but a quantitative comparison between the predicted results from these models has never been done. Although full-scale sorption processes are often carried out in fixed-beds, batch stirred-tank systems using simple and readily available mixing vessels are simple to operate and cost-effective and may find application in small- and medium-scale wastewater treatment facilities. Moreover, unlike synthetic ion exchange resins and activated carbon, many of the unconventional sorbent materials including, crustacean shells, are sheet-like and of irregular shape, which may lead to operational problems such as clogging or pressure drop fluctuations in a fixed-bed configuration. The virtues of these sorbents are thus better realized in a batch adsorber.

RATE MODELS

Four relatively simple rate models, namely, a second-order reversible reaction model, a second-order irreversible reaction model, a pseudofirst-order model, and the Elovich kinetic model, were used to quantify and predict the transient behavior of copper sorption on crab shell in a batch adsorber.

Second-Order Reversible Reaction Rate Model

The interaction that occurs between a metal cation and crab shell can be represented by a second-order reversible reaction of the form

$$M + A \underset{k_2}{\overset{k_1}{\rightleftarrows}} MA \tag{1}$$

where M is the metal ion in solution, A is the sorption site on the sorbent surface, and MA is the metal-sorbent complex. The two rate parameters, k_1 and k_2, are the second-order forward and first-order reverse rate constants, respectively. The rate of metal uptake by the sorbent in an interaction, described by Eq. 1, is given by

$$\frac{\mathrm{d}q}{\mathrm{d}t} = k_1 C(q_m - q) - k_2 q \tag{2}$$

where q and C represent the metal concentration in the solid and solution phase, respectively, at time t and q_m is the maximum sorption capacity of the sorbent. At equilibrium, $\mathrm{d}q/\mathrm{d}t$ equates to zero and Eq. 2 reduces to the classical Langmuir isotherm model:

$$q_\mathrm{e} = \frac{q_\mathrm{m} C_\mathrm{e}}{K_\mathrm{d} + C_\mathrm{e}} \tag{3}$$

where q_e and C_e are respectively the metal concentration in the solid and solution phase at equilibrium and K_d is the apparent dissociation constant given by

$$K_\mathrm{d} = \frac{k_2}{k_1} \tag{4}$$

Integrating Eq. 2 with appropriate initial conditions and applying a mass conservation equation gives the following analytical solution:[24]

$$\frac{C}{C_o} = 1 - \frac{1}{C_o}\frac{m}{v}\frac{(b+a)\left[1-\exp\left(-2a\frac{m}{v}k_1t\right)\right]}{\left[\frac{(b+a)}{(b-a)}-\exp\left(-2a\frac{m}{v}k_1t\right)\right]} \tag{5}$$

where C_o is the initial metal concentration, m is the mass of sorbent, and v is the volume of solution. The parameters a and b are defined as

$$a^2 = b^2 - C_o q_m \frac{v}{m} \tag{5a}$$

$$b = 0.5\left(C_o\frac{v}{m} + q_m + K_d\frac{v}{m}\right) \tag{5b}$$

The rate parameter k_1 is the only adjustable parameter in Eq. 5 if the Langmuir equilibrium parameters (q_m and K_d) are known because the other parameters (C_o, v, and m) are known to the experimenter.

Second-Order Irreversible Reaction Rate Model

Alternatively, the interaction that occurs between a metal cation and crab shell can be represented by a second-order irreversible reaction of the form

$$M + A \xrightarrow{k_3} MA \tag{6}$$

where k_3 is the second-order rate coefficient. The rate of change of the liquid phase metal concentration in an interaction, described by Eq. 6, is given by

$$\frac{dC}{dt} = -k_3C(C - C_e) \tag{7}$$

The analytical solution to Eq. 7 can be found by integration with appropriate initial conditions and is given by[20]

$$\frac{C}{C_o} = \frac{C_e}{C_o - (C_o - C_e)\exp(-C_e k_3 t)} \tag{8}$$

The two adjustable parameters in Eq. 8 are C_e and k_3. C_e can be estimated by solving Eq. 8a, which describes the equilibrium property of the adsorption process (q_e and C_e) in terms of a functional relationship f and Eq. 8b, which is a mass balance equation.

$$q_e = f(C_e) \tag{8a}$$

$$q_e = \frac{v}{m}(C_o - C_e) \tag{8b}$$

Eq. 8, therefore, contains one adjustable parameter (k_3).

Pseudofirst-Order Rate Model

A simple first-order rate model is the so-called Lagergren equation:[25]

$$\frac{dq}{dt} = k_4(q_e - q) \tag{9}$$

where k_4 is the pseudofirst-order rate coefficient. The integration of Eq. 9 with appropriate initial conditions gives the following solution:

$$q = q_e[1 - \exp(-k_4 t)] \tag{10}$$

Eq. 10 can be expressed in terms of the solution phase concentration using a mass balance equation:

$$\frac{C}{C_o} = 1 - \frac{q_e}{C_o}\frac{m}{v}[1 - \exp(-k_4 t)] \tag{11}$$

As described above, the equilibrium parameter q_e in Eq. 11 can be estimated by solving Eqs. 8a and 8b if the equilibrium property of the adsorption process can be quantified in terms of an isotherm equation. Eq. 11, therefore, contains one adjustable parameter (k_4).

Elovich Rate Model

The Elovich kinetic equation takes the following form:[23]

$$\frac{dq}{dt} = k_5 \exp(-k_6 q) \tag{12}$$

where k_5 and k_6 are the rate coefficients of the model. Integrating Eq. 12 with appropriate initial conditions and applying a mass balance equation, we have

$$\frac{C}{C_o} = 1 - \frac{1}{C_o}\frac{m}{v}\left[\frac{1}{k_6}\ln(t + t_o) - \frac{1}{k_6}\ln t_o\right] \tag{13}$$

where t_o equals $1/k_5k_6$. The adjustable parameters in Eq. 13 are the two rate coefficients k_6 and t_o.

MATERIALS AND METHODS

Deacetylation of Crab Shell

The deacetylation method of Coughlin et al.[2] was used in this work to convert chitin on the periphery of crab shell (*Portunus pelagicus*) to its deacetylated derivative, chitosan. The shell material was washed under running water and then rinsed with distilled water, followed by drying overnight at 60C. The dried shell was ground in a blender and sieved. Shell particles in the size range of 0.5 to 1.0 mm were first soaked in a 5% hydrochloric acid solution for 1 h at room temperature to remove calcium salts. After rinsing with distilled water, the decalcified crab shell particles were transferred to a 50% sodium hydroxide solution and incubated in a shaker at 90C for 1 h for deacetylation. After rinsing with distilled water and drying at 60C, the deacetylated shell particles were ready for use in copper sorption experiments.

Equilibrium Sorption Experiments

Batch equilibrium experiments were carried out using deacetylated crab shell. A series of flasks containing copper solutions of varying initial concentrations prepared from copper sulfate salt and a sorbent loading of 5 g/L were agitated in a rotary shaker at 200 rpm and 25°C for a period of 10 h, which was sufficient for the copper sorption process to reach equilibrium. The ionic strength of the solutions was adjusted to 0.05 M by adding an appropriate amount of sodium sulfate salt. Uptake experiments were conducted under constant pH values of 3, 4, 5, and 6, by adding sulfuric acid or sodium hydroxide at fixed time intervals. After equilibration, solution samples were filtered through a 0.45-μm membrane filter, acidified, and analyzed for residual copper concentration by an inductively coupled plasma spectrometer (Baird ICP 2000, USA). The amount of copper taken up by the crab shell sorbent in each flask was determined using a mass balance equation. Copper-free and crab shell-free blanks were used as controls.

Transient Sorption Experiments

Batch experiments for determination of the kinetics of copper sorption on deacetylated crab shell were carried out using a continuously stirred glass vessel with a diameter of 12.7 cm and a height of 24 cm. A motor was used to drive a six-blade Rushton turbine impeller with a diameter of 4.5 cm. Three baffles were spaced evenly around the vessel. The following experimental conditions were kept constant for the kinetic experiments: volume of solution = 1 L; initial copper concentration = 0.787 mmol/L (50 mg/L); sorbent dosage = 5 g/L; temperature = 25°C; and stirring speed = 300 rpm, to fully suspend and uniformly disperse the shell particles in the solution. The solution pH was maintained constant at 3, 4, and 6 during the sorption experiments using an automatic pH controller. Samples were withdrawn at fixed time intervals, filtered, acidified, and analyzed for residual copper concentration as described previously.

RESULTS AND DISCUSSION

Many of the methods reported for converting chitin in crustacean shells to chitosan are slow and consume significant amounts of reagents. A relatively rapid and mild deacetylation method was used in this work to develop chitosan on the outer surface of crab shell without substantially converting the interior regions of the shell. It has been demonstrated that metal uptake by partially converted crab shell was confined to the outer surface of the shell in batch studies with contact times as long as 12 h when apparent equilibrium was reached.[2] The metal ion removal ability of partially converted shell is thus similar to that of more exhaustively deacetylated material with interior binding sites that are most likely not accessible to metal ions in experiments with practical contact times of several hours.

A nonlinear least-squares regression program based on a combination of Gauss–Newton and Levenberg–Marquardt methods was used to fit the mathematical models described in this work to measured equilibrium and kinetic data. The fitting begins with an estimation of the values of model parameters and then keeps optimizing their values until the sum of squared residuals no longer decreases significantly.

Uptake Equilibrium

Figure 1 shows the fraction of copper removal plotted as functions of solution pH and initial copper concentration. The sorbent dosage was fixed at 5 g/L. As expected, the fraction of copper removal in a batch adsorber with a fixed sorbent dosage decreases with increasing initial copper concentration. At a fixed initial copper concentration, the fraction of copper adsorbed increases with increasing pH. In general, Figure 1 shows that the extent of copper sorption increases approximately linearly with pH in the range 3 to 6. The pH dependence of copper sorption on crab shell may be attributed to the affinity of chitosan for both copper ions and protons. X-ray

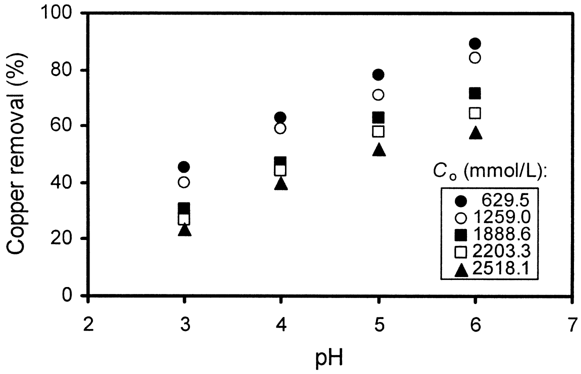

Figure 1. Experimental equilibrium data for copper on crab shell as functions of pH and initial copper concentration (C_o).

photoelectron spectroscopic studies demonstrated that the uptake of copper ions by chitosan is mainly effected via coordination with the amino groups (R–NH_2).[26] This copper–chitosan interaction can be represented by the following reversible reaction:

$$R - NH_2 + Cu^{2+} \leftrightarrow Cu(R - NH_2)^{2+} \tag{14}$$

It should be noted that the distribution of copper species calculated from the thermodynamic data describing copper hydrolysis and precipitation[27] indicates that Cu^{2+} is the predominant species in aqueous solution at $pH \leq 6$ under the experimental conditions employed in this work.

Because the pK_a of chitosan falls within the range of 6.2 to 6.8,[28] the amino groups in chitosan are protonated to varying degrees in the pH range of 3 to 6 according to the following equation:

$$R - NH_2 + H^+ \leftrightarrow R - NH_3^+ \tag{15}$$

According to Eqs. 14 and 15, low solution pH leads to a binary system with protons and copper ions competing for the finite number of binding sites. Lower sorption levels of copper at low pH, as shown in Figure 1 are thus likely due to the protonation of the amino groups, resulting in a smaller number of binding sites available for copper uptake. This hypothesis is supported by the observation that the pH of the batch experiment with an initial pH of 3 increased slightly during the sorption period, indicating an uptake of protons by the crab shell sorbent.

Constant pH sorption isotherms for copper measured at four different pH values are shown as symbols in Figure 2. Two commonly used isotherm equations, the two-parameter Langmuir model (Eq. 3) and the three-parameter Langmuir–Freundlich model (Eq. 16), were fitted to the isotherm data.

$$q_e = \frac{q_m C_e^{1/n}}{K_d + C_e^{1/n}} \tag{16}$$

where n is the Langmuir–Freundlich exponent. The fitted values of the equilibrium parameters are listed in Table 1. Isotherms calculated from these

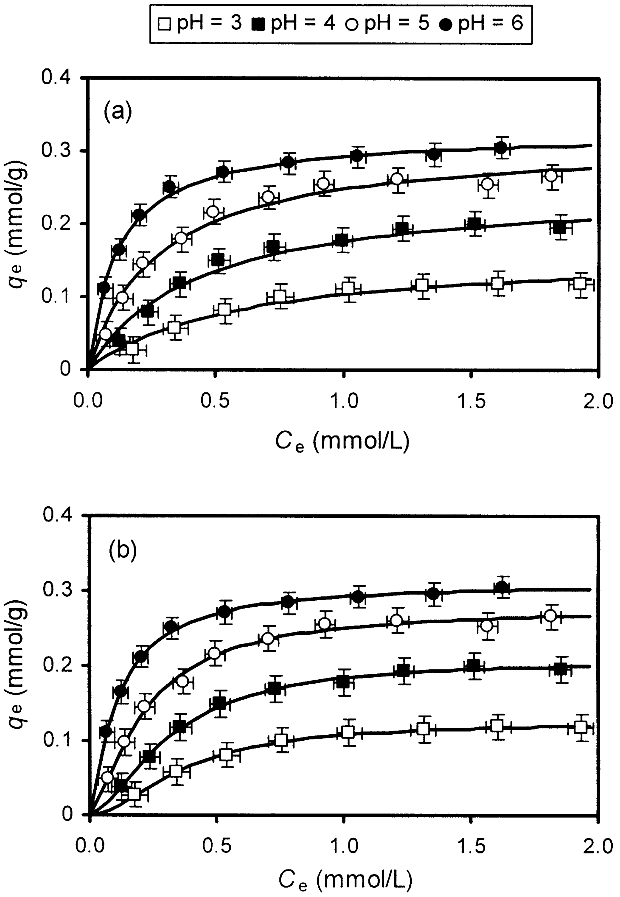

Figure 2. Equilibrium isotherms for copper on crab shell. Symbols: experimental data. Lines: (a) Langmuir model fits, Eq. 3 and (b) Langmuir–Freundlich model fits, Eq. 16.

Table 1. Langmuir (Eq. 3) and Langmuir–Freundlich (Eq. 16) parameters for the sorption of copper on crab shell.

	pH			
	3	4	5	6
Langmuir				
q_m (mmol/g)	0.163	0.252	0.316	0.327
K_d (mmol/L)	0.577	0.428	0.275	0.117
RMSE (mmol/g)	0.006	0.010	0.011	0.005
Langmuir–Freundlich				
q_m (mmol/g)	0.126	0.209	0.278	0.311
K_d (mmol/L)	0.167	0.139	0.108	0.064
n	0.551	0.595	0.690	0.803
RMSE (mmol/g)	0.002	0.003	0.006	0.003

best-fit parameters are shown as lines in Figure 2. The criterion for measuring the accuracy of Eqs. 3 and 16 is the root mean square error (RMSE):

$$\mathrm{RMSE} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(q_{\mathrm{e(expt,i)}} - q_{\mathrm{e(calc,i)}}\right)^2} \tag{17}$$

where the subscripts ''expt'' and ''calc'' denote experimental and calculated values, respectively, and N is the number of measurements. Table 1 lists the RMSE levels in the two models' estimates of q_e. It is evident that the Langmuir–Freundlich model outperformed the classical Langmuir model in terms of RMSE in all cases. This is not surprising as the Langmuir–Freundlich model, with three adjustable parameters, has greater flexibility in fitting experimental data than the Langmuir model with two adjustable parameters.

Although relatively simple isotherm models, such as the classical Langmuir model, have been widely used to describe metal sorption equilibria on a wide range of sorbent materials, these models, in general, do not incorporate pH effects. Consequently, each set of the Langmuir parameters q_m and K_d is only valid for a particular pH. It is desirable to establish the dependence of the isotherm parameters with pH, which will allow estimation of the isotherm for any given pH value. Figure 3 displays the variations of the best-fit Langmuir and Langmuir–Freundlich parameters with pH (symbols). A linear dependence of each equilibrium parameter with pH was observed. The lines in Figure 3 represent the correlations of the pH-dependent parameters to the following empirical expressions:

$$\text{Langmuir: } q_m = 0.056\mathrm{pH} + 0.014 \quad r^2 = 0.91 \tag{18}$$

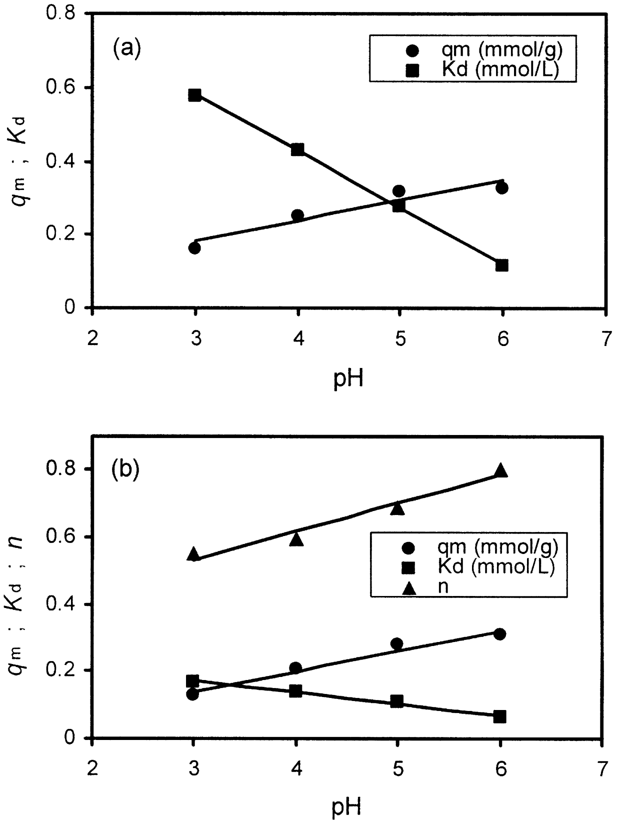

Figure 3. Variations of the best-fit (a) Langmuir and (b) Langmuir–Freundlich parameters with pH. Lines: linear regression fits.

$$\text{Langmuir: } K_d = -0.153\text{pH} + 1.039 \quad r^2 = 1.00 \tag{19}$$

$$\text{Langmuir} - \text{Freundlich: } q_m = 0.062\text{pH} + 0.050 \quad r^2 = 0.97 \tag{20}$$

$$\text{Langmuir} - \text{Freundlich: } K_d = -0.034\text{pH} + 0.273 \quad r^2 = 0.99 \tag{21}$$

$$\text{Langmuir} - \text{Freundlich: } n = 0.085\text{pH} + 0.277 \quad r^2 = 0.97 \tag{22}$$

The two isotherm models, with their parameters expressed as linear functions of pH, can be used to predict the equilibrium isotherms for the sorption of copper on crab shell within the pH range of 3 to 6.

An alternative to the correlation approach just described is the use of pH-sensitive isotherm models. Since protons compete with copper for binding sites on the crab shell, the sorption process may be viewed as a binary system and accordingly, the classical Langmuir model may be extended to a binary equilibrium model. An extended Langmuir model can be readily developed by assuming that no ions other than copper and proton can occupy the surface binding sites according to Eqs. 14 and 15 and that the binding sites are homogeneous. Such an approach yields the following equation, commonly known as the extended Langmuir model or the competitive Langmuir model, for copper sorption in the presence of protons:

$$q_e = \frac{q_m C_e}{K_d + C_e + \dfrac{K_d}{K_{dH}} H_e} \tag{23}$$

where H_e is the proton concentration in the solution phase at equilibrium and K_{dH} is the apparent dissociation constant for the reversible reaction described by Eq. 15. The extended Langmuir model is often used in the analysis of binary or multicomponent equilibrium data, owing to its simplicity. The extended Langmuir model, with three fitting parameters, was tested empirically by fitting Eq. 23 to the constant pH isotherms of Figure 2 and determining the best-fit values of the three parameters. The fitted parameters and RMSE levels are listed in Table 2. The same isotherm data of Figure 2 are shown as symbols in part (a) of Figure 4, where they are compared with the fits of the extended Langmuir model (lines). Satisfactory agreement was observed between model fits and experimental data obtained at pH 4 and 5.

Table 2. Extended Langmuir (Eq. 23) and Extended Langmuir–Freundlich (Eq. 24) parameters for the sorption of copper on crab shell.

	Extended Langmuir	Extended Langmuir–Freundlich
q_m (mmol/g)	0.297	0.333
K_d (mmol/L)	0.127	0.028
K_{dH} (mmol/L)	0.037	0.012
n	—	1.153
n_H	—	2.362
RMSE (mmol/g)	0.028	0.013

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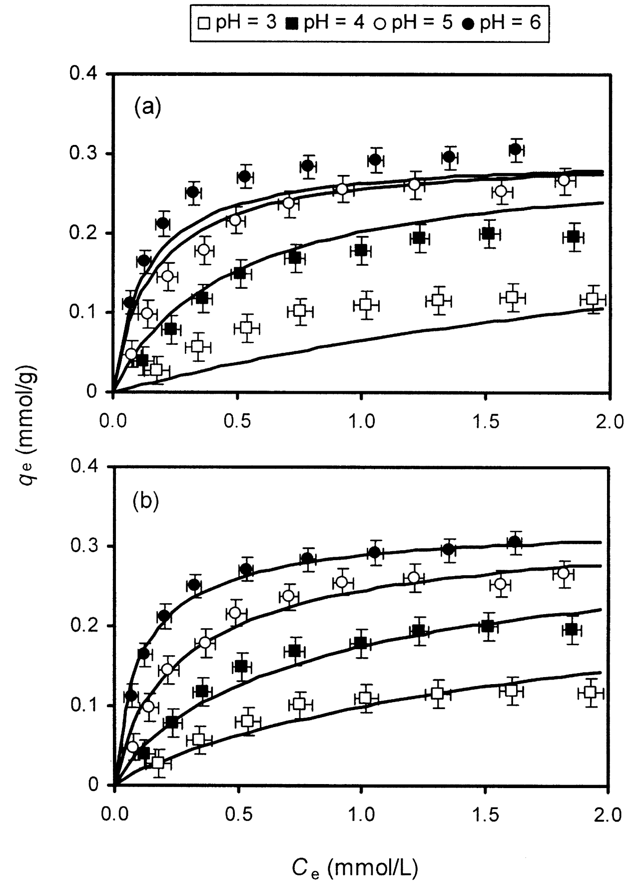

Figure 4. Equilibrium isotherms for copper on crab shell. Symbols: experimental data. Lines: model fits using (a) extended Langmuir model, Eq. 23 and (b) extended Langmuir–Freundlich model, Eq. 24.

However, the amount of copper adsorbed at pH 3 and 6 was higher than that predicted by the model.

When the extended Langmuir model proves inadequate in correlating binary equilibria, as observed in this work, its correlative capability may be enhanced by the introduction of a power law of the Freundlich form:

$$q_e = \frac{q_m C_e^{1/n}}{K_d + C_e^{1/n} + \dfrac{K_d}{K_{dH}} H_e^{1/n_H}} \tag{24}$$

where n and n_H are the Langmuir–Freundlich exponents for copper and proton, respectively. Eq. 24 is commonly called the extended Langmuir–Freundlich isotherm, which reduces to the extended Langmuir model when $n = 1$ and $n_H = 1$. The fitted values of the five adjustable parameters are listed in Table 2. Figure 4b shows that the agreement between isotherm data (symbols) and model fits (lines) is very good, much better than when the data were fitted to the extended Langmuir model (see Figure 4a). As mentioned previously, this situation was to be expected as the extended Langmuir–Freundlich model has five adjustable parameters instead of three. Note that various variants of the Langmuir model with pH-independent parameters have been proposed in the literature but these models are usually characterized by complex mathematical form with numerous adjustable parameters.[29,30]

Uptake Kinetics

Figure 5 shows the liquid phase transient concentration decay data obtained at a pH of 4 and a sorbent dosage of 5 g/L (symbols). The experimental transient profile indicates that ~90% of the total copper

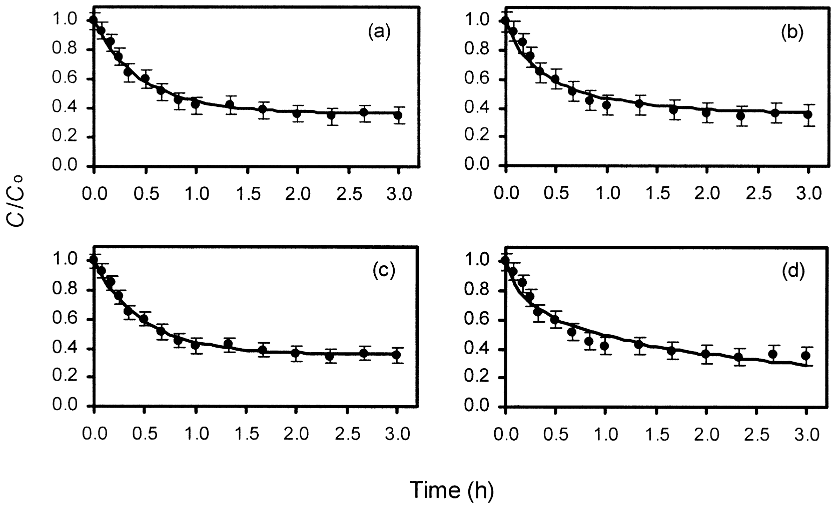

Figure 5. Transient profiles of copper removal by crab shell at pH = 4, $C_o = 0.787$ mmol/L, and $m/v = 5$ g/L. Symbols: experimental data. Lines: model fits calculated with best-fit rate coefficients obtained at pH 4 using (a) second-order reversible reaction model, Eq. 5; (b) second-order irreversible reaction model, Eq. 8; (c) pseudofirst-order model, Eq. 11; and (d) Elovich model, Eq. 13.

removal was achieved in the first hour of contact time. The experimental data are compared with solutions of the four rate models to determine their respective rate coefficients. Because the analytical expressions for the second-order reversible reaction, second-order irreversible reaction, and pseudofirst-order models reduce to essentially equilibrium models at sufficiently large times, the equilibrium parameters appearing in these expressions were determined from appropriate isotherm equations so that only the rate parameters were optimized in the curve-fitting exercise. Because Langmuir parameters have been incorporated within the analytical solution for the second-order reversible reaction model, the best-fit Langmuir q_m and K_d obtained at pH 4 (see Table 1), together with the other known operating conditions (C_o, m, and v) were used in the curve-fitting process. In the case of the second-order irreversible reaction and pseudofirst-order models, their equilibrium parameters were estimated by solving Eqs. 8a and 8b using the Langmuir–Freundlich model with its best-fit parameters (pH 4) listed in Table 1. Note that no equilibrium information is incorporated within the Elovich model. The fitted values of the rate coefficients (k_1, k_3, k_4, k_5, and k_6), estimated by fitting Eqs. 5, 8, 11, and 13 to the concentration decay data, are tabulated in the third column of Table 3. Note that the value of k_2 for the second-order reversible reaction model can be calculated from Eq. 4 once k_1 is known. The goodness of fit of each model to the transient data is shown by the lines in Figure 5 and is also indicated by the corresponding RMSE levels

Table 3. Rate coefficients for the sorption of copper on crab shell at pH 3, 4, and 6.

	pH		
	3	4	6
Second-order reversible reaction			
k_1 (L/mmol·h)	0.94	1.18	1.57
RMSE (mmol/g)	0.02	0.03	0.03
Second-order irreversible reaction			
k_3 (L/mmol·h)	2.46	3.62	5.33
RMSE (mmol/g)	0.02	0.04	0.02
Pseudofirst order			
k_4 (h^{-1})	1.58	2.05	2.45
RMSE (mmol/g)	0.02	0.02	0.04
Elovich			
k_5 (mmol/g·h)	0.16	0.40	1.11
k_6 (g/mmol)	37.73	33.29	31.50
RMSE (mmol/g)	0.03	0.05	0.03

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given in Table 3. Of the four models, the pseudofirst-order model gave very good agreement between experimental data and model fit, as can be seen in Figure 5c (RMSE = 0.02 mmol/g). Slight deviations were observed between measured data and model fit of the Elovich model, as shown in Figure 5d (RMSE = 0.05 mmol/g). It is generally difficult to distinguish among rate models on the basis of how well they fit transient data, as models based on different assumptions can often provide nearly identical fits, as observed in this study. Discrimination between the four rate models, therefore, requires more fundamental studies of the sorption process than afforded by interpretation of the observed rates.

Concentration decay profiles measured at pH 3 and 6 are shown in Figure 6 (symbols). As anticipated from the equilibrium study, Figure 6 shows that the extent of copper removal is strongly pH-dependent, which increases with increasing pH. Figure 6 shows comparisons between the experimental data (symbols) and predictions of the four rate models (lines) calculated using the best-fit rate coefficients obtained at pH 4 together with the equilibrium constants obtained at pH 3 or 6. It is evident that significant

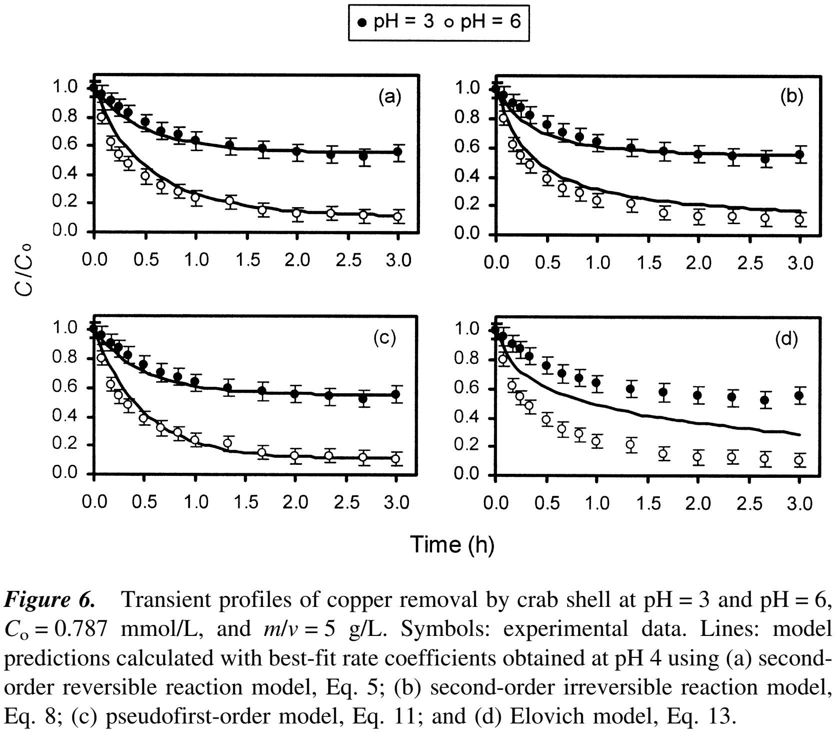

Figure 6. Transient profiles of copper removal by crab shell at pH = 3 and pH = 6, $C_o = 0.787$ mmol/L, and $m/v = 5$ g/L. Symbols: experimental data. Lines: model predictions calculated with best-fit rate coefficients obtained at pH 4 using (a) second-order reversible reaction model, Eq. 5; (b) second-order irreversible reaction model, Eq. 8; (c) pseudofirst-order model, Eq. 11; and (d) Elovich model, Eq. 13.

deviations were observed with the Elovich model, as shown in Figure 6d (RMSE = 0.17 and 0.21 mmol/g for pH 3 and 6, respectively). The deficiency of the Elovich model stems largely from the fact that, unlike the other three models, equilibrium information is not incorporated within the structure of the model. In fact, the prediction shown in Figure 6d is identical to that of Figure 5d. It is obvious that the Elovich model cannot be used to predict the pH dependence of copper sorption on crab shell unless its rate coefficients k_5 and k_6 are optimized, as discussed later.

For the other three models, Figure 6a, b, and c show that it is possible to obtain a satisfactory correspondence between the shapes of the experimental profiles and predicted curves, especially at the later stage of the transient profiles when apparent equilibrium was established. This means that the final removal levels in the transient experiments are equal to the removal levels predicted by the equilibrium isotherms. This is not surprising as the appropriate equilibrium parameters obtained at pH 3 or pH 6 were used in the calculations of the predictions of all three models. However, systematic discrepancies between experimental data and model predictions of all three models were found in the initial parts of the transient profiles: the predicted concentration decay curves of all three models are slightly below the experimental values obtained at pH 3 (RMSE = 0.03, 0.05, and 0.03 mmol/g for the second-order reversible reaction, second-order irreversible reaction, and pseudofirst-order models, respectively) while the reverse is the case for the sorption of copper at pH 6 (RMSE = 0.06, 0.07, and 0.05 mmol/g for the second-order reversible reaction, second-order irreversible reaction, and pseudofirst-order models, respectively).

One possible explanation for the discrepancies is that competition between copper ions and protons for binding sites has an adverse effect on the kinetics of copper removal. Higher concentrations of protons at low pH levels imply higher competition, leading to slower rates of copper removal. As a result, in the case of copper sorption at pH 3 the three models predicted lower C/C_o values than the measured data because the rate coefficients obtained at pH 4 underestimated the effect of competitive binding. In the case of copper sorption at pH 6, where competitive binding is minimal due to the relatively low concentrations of protons, the rate coefficients obtained at pH 4 overestimated the adverse effect of competitive binding on the kinetics of copper removal, causing the models to predict higher C/C_o values than the experimental readings. As discussed previously, all three models take into account the competitive effect on the equilibrium behavior through the use of the equilibrium parameters obtained at pH 3 or 6, resulting in good agreement between predictions and measured data at sufficiently large times when equilibrium was established in the batch adsorber.

The effect of pH on the sorption kinetics suggests the existence of competitive binding between copper ions and protons, which limits the sorption efficiency. Since the rate models used to generate the predictions neglect competition between protons and copper for binding sites during the transient sorption stage, the predictive power of the rate models may be improved by taking into consideration the reaction kinetics of chitosan and protons as described by Eq. 15. This would require the use of more complicated binary rate models that would in turn, require additional experimental work for model calibration and validation.

One alternative approach to achieving better agreement of the data is to establish the empirical relationships between the rate coefficients of these relatively simple rate models and pH. Solutions of the four rate models were matched to the experimental data obtained at pH 3 and 6 by adjusting the respective rate coefficients. The best-fit values of the rate coefficients together with the corresponding RMSE levels are summarized in columns 2 and 4 of Table 3. Figure 7 displays the goodness of the resulting fits (lines). In all cases, good agreement between experimental readings and model fits

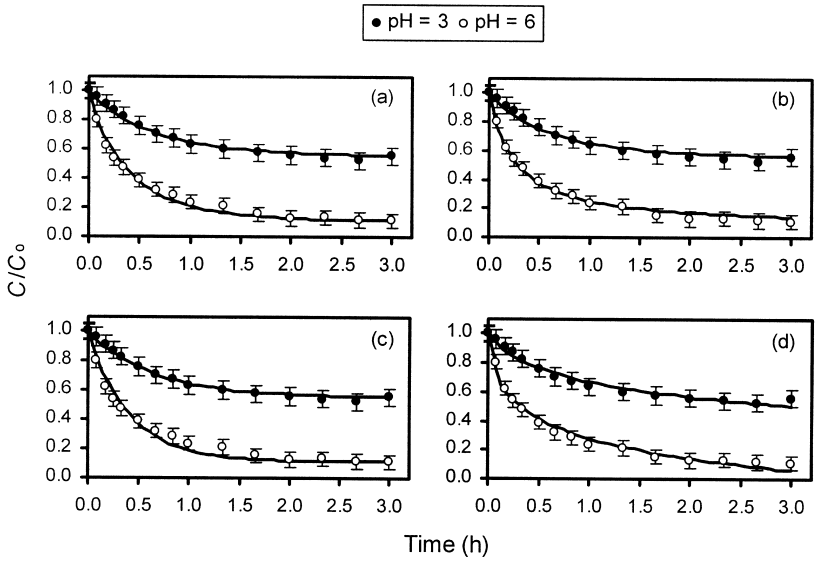

Figure 7. Transient profiles of copper removal by crab shell at pH = 3 and pH = 6, $C_o = 0.787$ mmol/L, and $m/v = 5$ g/L. Symbols: experimental data. Lines: model fits calculated with best-fit rate coefficients obtained at pH 3 and 6 using (a) second-order reversible reaction model, Eq. 5; (b) second-order irreversible reaction model, Eq. 8; (c) pseudofirst-order model, Eq. 11; and (d) Elovich model, Eq. 13.

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was observed. Table 3 indicates that k_1, k_3, k_4, and k_5 increase while k_6 decreases with increasing pH. The variations of the best-fit rate coefficients tabulated in Table 3 with pH can be described by the following empirical linear expressions:

$$k_1 = 0.208\text{pH} + 0.329 \quad r^2 = 0.99 \tag{25}$$

$$k_3 = 0.942\text{pH} - 0.279 \quad r^2 = 0.99 \tag{26}$$

$$k_4 = 0.277\text{pH} + 0.826 \quad r^2 = 0.95 \tag{27}$$

$$k_5 = 0.322\text{pH} - 0.839 \quad r^2 = 0.99 \tag{28}$$

$$k_6 = -1.908\text{pH} + 42.441 \quad r^2 = 0.83 \tag{29}$$

It is evident that only the equation for k_6 yields a regression coefficient $r^2 < 0.90$, indicating that the variation of k_6 with pH is considerably more scattered. For the three models characterized by a single rate coefficient (second-order reversible reaction, second-order irreversible reaction, and pseudofirst order), the rate coefficient tends to decrease with decreasing pH to compensate for the competitive effect of protons on the sorption of copper. Note that there is a particularly large drop in k_3, the rate coefficient of the second-order irreversible reaction model, on reducing the solution pH. Note that the second-order reversible reaction model contains two rate coefficients but one of which (k_2) has been factored out of the final analytical solution expression (Eq. 5) through mathematical manipulation. Although Eqs. 25 through 29, along with the respective rate models are useful for predicting the effect of pH on the transient behavior of copper sorption within the pH range of 3 to 6, they should not be used for extrapolation purposes due to the empirical nature of the equations. Cheung et al.[21,22] also found a linear dependence of the rate coefficients of the Elovich model on system variables, such as the initial metal concentration and the mass of sorbent, for the sorption of copper, zinc, and cadmium on bone char. From an engineering viewpoint, despite the need to correlate the rate coefficients with system variables, these relatively simple models with analytical solutions are especially useful for the preliminary design and optimization of batch adsorbers due to their mathematical simplicity.

CONCLUSION

Given the likely low costs of obtaining crab shell waste and mild chemical treatment, partially converted crab shell is an attractive and cost-competitive sorbent for the pretreatment or polishing of industrial wastewater containing toxic metal ions in trace quantities. In this work, batch equilibrium and transient data for the sorption of copper on partially converted crab shell as a function of solution pH were obtained. The extent of copper removal increases on raising solution pH. This can be explained on the basis of a decrease in competition between protons and copper ions for the amino groups of chitosan in the crab shell sorbent. Four isotherm models (Langmuir, Langmuir–Freundlich, extended Langmuir, and extended Langmuir–Freundlich) were used to account for the measured equilibrium data. The best results were obtained by optimizing and correlating the equilibrium parameters of the Langmuir–Freundlich model and the extended Langmuir–Freundlich model with solution pH.

Batch transient experiments indicate that the sorption rates are fairly rapid, with 90% of the total copper removal occurring within the first hour of contact time. The experimental transient data were fitted to four rate models (second-order reversible reaction, second-order irreversible reaction, pseudofirst-order, and Elovich). The major advantage of these models, which have either one or two rate coefficients, is their mathematical simplicity. It is not possible to use a unique value of the rate coefficient to account for the effect of pH on the sorption kinetics. A linear correlation of the rate coefficients with pH was found. To predict the effect of pH on the transient behavior of copper sorption on crab shell using any one of the models, an appropriate rate coefficient corresponding to a particular pH value must, therefore, be used in the model calculation. An appropriate rate model should give correct predictions of both transient and equilibrium data. Of the four models investigated here, only the Elovich model does not possess this feature. The principal finding of this work is that modeling approaches using simplified rate models can produce useful results provided that equilibrium information is embodied within the model structure and the dependence of rate coefficients on system variables such as pH is properly accounted for in the modeling strategy.

NOMENCLATURE

a	parameter defined in Eq. 5a (mmol/g)
A	sorption site on sorbent surface

b	parameter defined in Eq. 5b (mmol/g)
C	metal concentration in the solution phase at time t (mmol/L)
C_e	metal concentration of solution phase at equilibrium (mmol/L)
C_o	initial metal concentration of solution phase (mmol/L)
H_e	proton concentration of solution phase at equilibrium (mmol/L)
k_1	forward rate coefficient of second-order reversible reaction model (L/mmol·h)
k_2	backward rate coefficient of second-order reversible reaction model (h^{-1})
k_3	rate coefficient of second-order irreversible reaction model (L/mmol·h)
k_4	rate coefficient of pseudofirst-order model (h^{-1})
k_5	rate coefficient of the Elovich model (mmol/g·h)
k_6	rate coefficient of the Elovich model (g/mmol)
K_d	apparent dissociation constant for copper (mmol/L)
K_dH	apparent dissociation constant for proton (mmol/L)
m	mass of sorbent (g)
M	metal ion in the solution phase
MA	metal–sorbent complex
n	Langmuir–Freundlich exponent for copper
n_H	Langmuir–Freundlich exponent for proton
N	number of experimental measurements
q	metal concentration in the sorbent phase at time t (mmol/g)
q_e	metal concentration of sorbent phase at equilibrium (mmol/g)
q_m	maximum sorption capacity of the sorbent (mmol/g)
r^2	regression coefficient
t	time (h)
t_o	$1/k_5k_6$ (h)
v	volume of solution (L)

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