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BIOSORPTION OF Cu FROM FERRUGINOUS WASTEWATER BY ALGAL BIOMASS

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Abstract—The biosorbent prepared from *Sargassum* algal biomass binds approximately 2.3 meq/g of metal cations from water by ion exchange. The values of ion exchange equilibrium constants showed that the affinities of metals towards the biosorbent decrease in the following order Cu > Ca > Fe. A flow-through sorption column was used to continuously and selectively remove Cu^{2+} from the feed containing Cu and Fe ions. A chromatographic effect in the column performance caused by different sorption affinities of the metal ions studied was successfully predicted by the equilibrium column model. The biosorbent saturated with Cu was regenerated with 0.1 M HCl. When Fe(III) was present in the mixed feed solution as suspended solids (SS) the column removed Cu^{2+} by biosorption and Fe(III) solids by in-depth filtration while producing effluent free of heavy metals from the feed containing 25 mg/l of Cu^{2+} and Fe(III) as SS in the concentration range of 15–40 mg/l. Effective copper removal/recovery from ferruginous wastewater using *Sargassum* biosorbent was demonstrated. © 1998 Elsevier Science Ltd. All rights reserved

Key words—Cu(II) removal, biosorption, *Sargassum*, ion exchange

NOMENCLATURE

A, B	divalent metal species
C(M)	concentration of metal M in the liquid (meq/l)
C_0(M)	concentration of metal M in the feed to a flow-through column (meq/l)
C_0	total normality of the feed to a flow-through column (meq/l)
C(M)/C_0(M)	relative concentration in column effluent
DO	dissolved oxygen
F	volumetric flowrate (m^3/h)
K_{AB}	equilibrium ion exchange constant defined by equation 5
q(M)	equilibrium uptake of metal M by the biosorbent (meq/g)
Q	concentration of metal binding sites in the biosorbent (meq/g)
T	dimensionless time in the ECM model
t	time (h)
V_C	volume of the packed-bed (m^3)
x_A	equilibrium equivalent fraction of species A in the liquid
y_A	equilibrium equivalent fraction of species B in the sorbent
ρ_b	biomass packing density (g/m^3)

INTRODUCTION

The conventional process of heavy metal removal from industrial wastewater involves chemical precipitation of metals usually by lime followed by settling of the metal precipitates in a pond and/or a clarifier. The major shortcomings of the conventional treatment include (1) low efficiency at low concentration of heavy metals and (2) expensive handling and safe disposal of toxic sludges. Innovative methods of heavy metal removal including biosorption (Volesky, 1990), sorption onto purified biopolymers (Jang *et al.*, 1995), adsorptive filtration using coated sands (Benjamin *et al.*, 1996), and adsorption on magnetic iron oxides (Chen *et al.*, 1991), have been investigated in an ongoing effort to develop a better treatment for wastewater containing toxic heavy metals.

Biosorption is a process which employs inexpensive dead biomass of algae (Kratochvil *et al.*, 1997), fungi (Fourest and Roux, 1992) or peat moss (Jeffers *et al.*, 1991) to sequester heavy metals from aqueous solutions. The major advantages of biosorption include (1) low cost, (2) high efficiency of heavy metal removal from diluted solutions, (3) regeneration of the biosorbent and (4) the possibility of metal recovery. It has been reported that the biomass of brown algae of the *Sargassum* family possesses a metal binding capacity superior to other sorbents both organic and inorganic (Holan *et al.*, 1993; Holan and Volesky, 1995; Volesky and Holan, 1995; Kratochvil *et al.*, 1997).

Usually, many types of aquatic pollution caused by heavy metals also contain iron as one of the elements. Recently, the biosorption equilibrium of a Cd–Fe system was studied and a methodology

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allowing the evaluation of interferences in biosorption was introduced (Figueira *et al.*, 1997).

The objective of this work was to investigate the interference of iron in the biosorption of copper by *Sargassum* biosorbent, taking into account the speciation of iron in water.

Iron speciation in water

Iron typically enters bodies of water in the form of ferrous iron (Fe^{2+}) which can be oxidized to ferric iron (Fe^{3+}) by the oxygen dissolved in water according to equation (1). The rate of the oxidation reaction (equation (1)) depends primarily on the pH and on the level of dissolved oxygen (DO) in water. Consequently, due to a lack of DO, Fe^{2+} is the predominant form of iron in groundwater and in deep water reservoirs. At pH < 4 and a relatively low DO, the reaction in equation (1) is very slow (Stumm and Morgan, 1981). At pH > 4, however, Fe^{2+} ions oxidize quickly to Fe^{3+} ions which then react with water according to equation (2) producing ferric hydroxide precipitate and acidity.

$$Fe^{2+} + 1/4O_2 + H^+ = Fe^{3+} + 1/2H_2O \quad (1)$$

$$Fe^{3+} + 3H_2O = Fe(OH)_3(s) + 3H^+ \quad (2)$$

If the pH drops below 3, the ferric ions cease to precipitate and remain in water in partially hydrolyzed forms (Dudeney *et al.*, 1994). In practice, the pH is usually raised above pH 3 by dilution through a discharge of ferruginous effluents into streams and/or stabilization ponds (Dudeney *et al.*, 1994; Gazea *et al.*, 1996). It has been demonstrated that certain types of Fe(III) precipitates can undergo a reductive dissolution in the presence of organic matter according to (Vile and Wieder, 1993):

$$\text{Fe(III)(s)+soluble organics} = Fe^{2+} + \text{oxidized soluble organics} \quad (3)$$

A typical example of an organic substance known to be reducing Fe(III) particles is fulvic acid (Deng and Stumm, 1993).

In addition to iron and acidity, toxic heavy metals including Cu, Zn and Cd are often present in industrial effluents. The toxic heavy metals do not react with dissolved forms of iron, however, their cations are capable of sorbing onto the iron precipitate (Gutzman and Langford, 1993). A variety of conditions including the water source, the pH and the DO level, bring about a diversity of effluents with metal content varying from traces to grams per liter levels (Gazea *et al.*, 1996).

Theory of biosorption

Recently, several researchers have independently concluded that the major mechanism of heavy metal uptake by algae (Crist *et al.*, 1990; Kratochvil *et al.*, 1995), fungi (Fourest and Roux, 1994) and peat moss (Spinti *et al.*, 1995) is ion exchange. Furthermore, it has been demonstrated that algal bisorbents, similar to ion exchange resins, can be prepared in different ionic forms such as H-form and Ca-form (Kratochvil *et al.*, 1997). Consequently, ion exchange models have been introduced to fit and interpret the data obtained from both equilibrium and dynamic biosorption experiments (Kratochvil *et al.*, 1997; Schiewer and Volesky, 1997). A binary ion exchange system containing divalent metal ions A and B may be described by the following exchange reaction

$$A^{2+} + (B - \text{biomass}) \Leftrightarrow B^{2+} + (A - \text{biomass}) \quad (4)$$

The corresponding equilibrium constant is defined as

$$K_{AB} = \frac{q_A C_B}{q_B C_A} \quad (5)$$

where q_A and q_B are the equilibrium uptakes (meq/g) and C_A and C_B are the equilibrium concentrations of species A and B in the liquid (meq/l), respectively. The value of the equilibrium constant K_{AB} can be determined from the slope of the plot of q_A/q_B versus C_A/C_B. The overall binding capacity Q (meq/g of dry biosorbent) is given by the density of the functional groups in the sorbent and can be expressed as

$$Q = q_A + q_B \quad (6)$$

The total normality of the solution C_0 is given by

$$C_0 = C_A + C_B \quad (7)$$

By substituting equation (6) into equation (5), q_B can be eliminated from equation (5) and the following expressions for q_A/Q can be obtained

$$\frac{q_A}{Q} = \frac{1}{1 + (C_B/K_{AB}C_A)} = \frac{1}{1 + \bar{k}C_B} \quad (8)$$

where $\bar{k} = 1/K_{AB}C_A$. Since q_A/Q represents the fraction of the binding sites occupied by A, equation (8) may be used to evaluate the decrease of the equilibrium uptake of the species A by the biosorbent due to the presence of species B. Equation (8) shows that when $C_B = 0$, $q_A/Q \cong 1$, regardless of the absolute value of the final concentration of A, C_A. This distinguishes ion exchange from chemisorption and/or physical sorption known to occur on activated carbon, whereby q_A/Q is always a function of C_A. Furthermore, equation (8) shows that for a fixed value of C_A, the q_A/Q is a hyperbolic function of C_B. Equation (8) may be transcribed using the following dimensionless variables

$$x_A = \frac{C_A}{C_0}; \qquad x_B = \frac{C_B}{C_0}; \qquad y_A = \frac{q_A}{Q} \quad (9)$$

yielding equation (10) which represents the binary ion exchange isotherm for the system

$$y_A = \frac{1}{1 + (x_B / K_{AB} x_A)} \quad (10)$$

Since y_A, x_B and K_{AB} are all dimensionless, equation (10) represents the most generalized description of the equilibrium for binary systems.

Equilibrium column model (ECM) for fixed-bed columns. The ECM has been developed to describe the competitive ion exchange in columns (Klein *et al.*, 1967). The principal assumptions of the ECM are (1) constant composition of the feed, (2) neutralization, complex formation and precipitation do not occur in the exchanger bed, (3) homogeneous presaturation of the biosorbent/resin and (4) negligible mass transfer resistance for ions diffusing from the bulk of the liquid into the biosorbent/resin particle. Although knowledge of the mass transfer resistance is important for sizing the columns, the ECM has proved to be useful for assessing the technical and economic feasibility of ion exchange processes (Klein *et al.*, 1967).

Based uniquely on the known values of equilibrium ion exchange constants for a given system, the ECM describes a column as being divided into several sections of constant composition called plateaus, connected by zones of varying composition called transitions. The transitions are further classified as either abrupt (constant-pattern) or gradual (proportionate-pattern). The rules derived for the ECM by Klein *et al.* (1967) and Tondeur and Klein (1967) help to identify the transition type and impose restrictions on the occurrence of species in any given plateau or transition.

For the special case of a column packed with a biosorbent/resin in the B-form and receiving a feed containing species A and C, the rules of the ECM predict that a pattern similar to the one shown in Fig. 1 will develop in the column, provided that the affinities of the species toward the biosorbent decrease in the following order A > B > C. The concentration histories of the species A, B and C in the column effluent form a mirror image of the concentration pattern shown in Fig. 1. The ECM uses exclusively dimensionless variables and hence the composition in liquid is always expressed as x and time as the dimensionless throughput, T, defined by equation 11:

$$T = \frac{C_0 F t}{\rho_b Q V_C} \quad (11)$$

The precise compositions and locations of the plateaus and transitions are determined as follows. First, the composition in the biosorbent in the first plateau, i.e. y_{A1} and y_{C1}, is calculated from the known composition of the feed, e.g. x_{A1} and x_{C1}, using equation 10. Next, the composition of the second plateau, i.e. x_{B2}, x_{C2}, y_{B2} and y_{C2}, and the dimensionless time T_{12} corresponding to the abrupt transition, are calculated from the set of equations formed by the modified equations in equations (5)–(7) and the ECM equations in equations (12) and (13):

$$K_{BC} = \frac{y_{B2} x_{C2}}{y_{C2} x_{B2}} \quad (5 \text{ modified})$$

$$x_{B2} + x_{C2} = 1 \quad (6 \text{ modified})$$

$$y_{B2} + y_{C2} = 1 \quad (7 \text{ modified})$$

$$T_{12} = \frac{y_{A1}}{x_{A1}} \quad (12)$$

$$T_{12} = \frac{y_{C2} - y_{C1}}{x_{C2} - x_{C1}} \quad (13)$$

Finally, x_C as a function of time T in the gradual transition is calculated using the ECM equation:

$$T = \frac{dy_C}{dx_C} = \frac{K_{BC}}{[x_C + K_{BC}(1 - x_C)]^2} \quad (14)$$

The origin and derivation of the ECM equations in equations (11)–(14) is discussed in detail in the work by Klein *et al.* (1967), Tondeur and Klein (1967) and Helfferich (1967a,b).

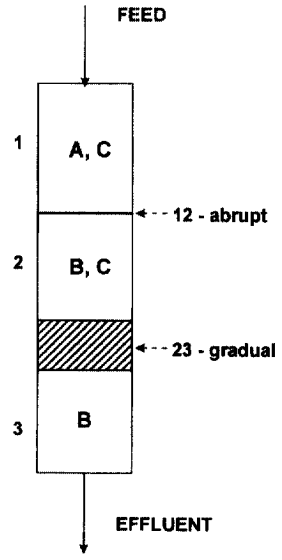


Fig. 1. Fundamentals of the equilibrium column model: Plateau sections of the sorption column for species A, B and C.

MATERIALS AND METHODS

Biosorbent

Sargassum seaweed biomass was collected beach-dried on the Gulf Coast of Florida in August 1995. In the laboratory, the biomass was first protonated with 0.2 M H_2SO_4 followed by a rinse with distilled water. Next, the conversion of the protonated biomass to Ca-biomass was carried out with a 1.2 g/l solution of $Ca(OH)_2$. The pH of the spent wash solution was 6.5. Finally the Ca-biomass was dried in the oven overnight at 50°C.

Sorption equilibrium experiments

Distilled water was purged with nitrogen gas for 5 min and solutions of Fe^{2+} and Cu^{2+} in this water were prepared using the respective sulfate salts of the metals. Approximately 200 mg of dried Ca-biomass was combined with 50 ml of metal solutions at pH 3.8 adjusted with H_2SO_4 in 200 ml Erlenmeyer flasks. The flasks were capped, placed on a shaker and left to equilibrate until the metal concentrations in the liquid reached new constant values (within 4 h). Uptakes of metals were determined from the difference of metal concentrations in the initial and final solutions. Seven sample flasks containing biomass and metal solution were run in duplicates. In addition blank flasks containing only metal solution were run simultaneously with the sample flasks in order to determine the amount of Fe^{2+} oxidized to Fe(III) over the course of equilibration. The results revealed that this amount was negligible.

Column experiments

Dry Ca-biomass was packed in a 50 cm long column of 2.5 cm internal diameter, yielding an approximate packing density of 200 g/l. The column was then slowly flooded with water from the bottom. Synthetic metal solutions of $FeSO_4$ and $CuSO_4$ and $Fe_2(SO_4)_3$ and $CuSO_4$ were prepared in distilled water and acidified with H_2SO_4 to pH 3.0 and 2.1, respectively. During the experiments, solutions were pumped from a 40 l storage tank to the column through a 1.5 l stirred tank. The pH of the liquid in the stirred tank was being adjusted to pH 4 using NaOH while nitrogen gas was continuously bubbled through the contents of the tank to prevent Fe^{2+} oxidation. The metal solution was fed into the column from the top at a rate of 2 and 3 cm/min (0.5 and 0.75 gpm/ft^2). Samples of the column feed were withdrawn from the stirred tank at the beginning and at the end of each sorption experiment. The amount of suspended solids (SS) in a feed was determined from the difference of Fe_{total} concentration in aliquots of samples filtered through 45 μm chromatographic filters and unfiltered acidified aliquots of the same samples. Samples of the column effluent were collected using a fraction collector. Pressure drop across the column was measured with a pressure transducer.

Metal analysis

The concentrations of Cu and of Fe_{total} were determined by atomic absorption (Perkin-Elmer 3100). The concentration of Fe^{2+} was measured according to the Penny–Knop method (Vogel, 1961) by titrating aliquots of samples with potassium dichromate in excess of phosphoric acid while using diphenylamine as an indicator.

Total Organic Carbon

Total organic carbon (TOC) was measured using a TOC analyzer (Dohrman DC-80) by both combustion and UV-persulfate methods. All samples were acidified with concentrated H_2SO_4 prior to analysis.

RESULTS AND DISCUSSION

According to equation (5), the sorption equilibrium data for the two binary systems Fe–Ca and Fe–Cu were plotted as q_A/q_B versus C_A/C_B, where A and B represented Fe and Ca, and Cu and Fe in the two plots, respectively. Both plots featured seven datapoints to which a straight lines were successfully fitted (Fe–Ca: $y = 0.3028x$; Fe–Cu: $y = 6.7341x$) passing through the origins of the plots yielding, (Fe–Ca: $R^2 = 0.97$; Fe–Cu: $R^2 = 0.99$).

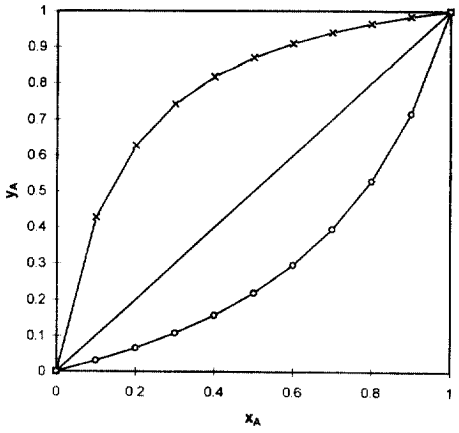


Fig. 2. Binary ion exchange isotherms calculated by using equation 10: (×) A = Cu, B = Fe, $K_{AB} = 6.7$; (○) A = Fe, B = Ca, $K_{AB} = 0.3$.

This indicated that the ion exchange model provides a relatively good description of the biosorption of the heavy metals by the algal biomass. The values of ion exchange equilibrium constants determined from the slopes of the above mentioned straight lines were $K_{FeCa} = 0.3$ and $K_{CuFe} = 6.7$ for the Fe–Ca and Fe–Cu systems, respectively. Based on equation (5), the value of the constant $K_{CuCa} = 2.04$ was calculated as the product of K_{CuFe} and K_{FeCa}. The equilibrium constants defined by equation (5) are related to Gibbs free energy of ion exchange reactions (equation (4)) and hence the values of the constants reflect the relative affinities of the metals towards the binding groups in the *Sargassum* biomass. Consequently, the metals can be sorted in the order of descending affinity based on the values of the equilibrium constants as follows: Cu > Ca > Fe.

Furthermore, once the equilibrium constants K_{FeCa} and K_{CuFe} are determined, the ion exchange isotherms represented by equation 10 can be plotted for the binary systems in question using the dimensionless coordinate system [y_A, x_A] as shown in Fig. 2. The diagonal line in Fig. 2 represents the hypothetical case of an equilibrium where the composition of A in the liquid and in the sorbent are the same thereby indicating that the sorbent is not selective for either of the components of the binary system. Clearly, the sorbent is selective when it sorbs preferentially either the species A or the species B from the binary mixture. The former and the latter case are represented by equilibrium isotherms of A which pass above and below the diagonal line, respectively, in the [y_A, x_A] coordinate system. It can be seen from Fig. 2 that both Cu and Ca are sorbed preferentially from their respective binary mixtures with Fe over the entire concentration interval. Furthermore, equation (5) shows that for equimolar binary mixtures of Fe and Cu, i.e. when $x_{Fe} = x_{Cu} = 0.5$, the value of the equilibrium constant expresses the ratio of the metal uptakes $K_{CuFe} = q_{Cu}/q_{Fe}$. Hence, the *Sargassum* bio-

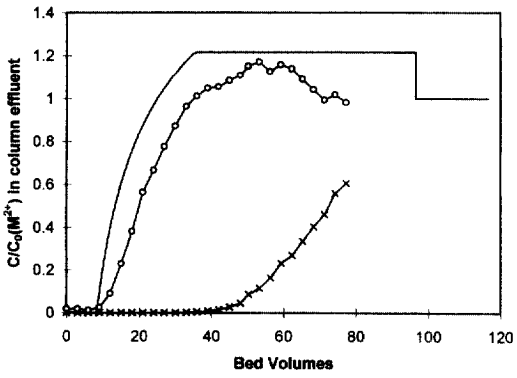
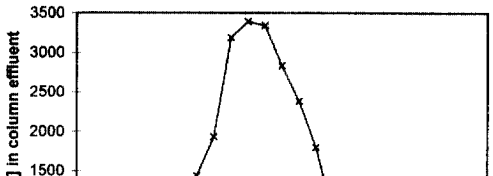


Fig. 3. Model breakthrough curve of Fe^{2+} and experimental breakthrough curves of Fe^{2+} and Cu^{2+}: (×) experiment Cu^{2+}; (○) experiment Fe^{2+}; (—) model Fe^{2+}; bed volume = 200 ml; flowrate = 2 cm/min; pH of the feed = 4.0; $C_0(Cu^{2+}) = C_0(Fe^{2+}) = 4$ meq/l.

mass equilibrated with an equimolar mixture of Fe^{2+} and Cu^{2+} is expected to bind approximately 6.7 times more of Cu than Fe.

The natural selectivity of the biomass for Cu over Fe is well reflected in the results obtained using the flow-through column. Figure 3 displays the concentrations of Fe^{2+} and Cu^{2+} in the column effluent as a function of time for the sorption experiment during which the column packed with *Sargassum* biosorbent in Ca-form was fed with an equimolar mixture of Cu^{2+} and Fe^{2+}. As can be seen in Fig. 3, Fe^{2+}, due to its low affinity, broke through the column much faster than Cu^{2+}. At approximately the 35 bed volume mark, the concentration of Fe^{2+} in the column effluent plotted in Fig. 3 reached the level of Fe^{2+} in the feed, i.e. $(C/C_0) = 1$. Hence, thereafter, Fe^{2+} was no longer taken up by the biosorbent. The fact that C/C_0 for Fe^{2+} continued rising above 1 after 35 bed volumes in Fig. 3 may be explained by the ion exchange between Cu and Fe whereby Cu^{2+} from the solution was displacing Fe bound to the biosorbent. Since no more Fe^{2+} was being sorbed from the liquid beyond 35 bed volumes, the released Fe^{2+} increased the overall concentration of Fe^{2+} in the effluent above the level present in the column influent. This overshoot of Fe^{2+} in the column effluent was further investigated by calculating C/C_0 for Fe^{2+} using the ECM by solving equations (5)–(14), introduced earlier, with A, B and C being Cu, Ca and Fe, respectively. As can be seen in Fig. 3, the model curve in Fig. 3 is steeper than the experimental breakthrough curve for Fe^{2+}. A column sorption model (Tan and Spinner, 1994) used successfully in the recent continuous-flow copper biosorption study (Kratochvil *et al.*, 1997) could accommodate the process mass transfer aspects. However, the applicability of this model hinges on the knowledge of mass transfer parameters which may depend on (a) the composition in the liquid (Helfferich, 1965), (b) the pretreatment of the biomass and (c) the number of completed sorption/desorption cycles, i.e. biomass aging (Kratochvil *et al.*, 1997).

Desorption of the metals deposited in the biosorbent is likely (Kratochvil *et al.*, 1997) and the determination of desorption dynamics represents a crucial information for biosorption process design and for metal recovery assessment. Figure 4 shows the elution peaks of Cu and Fe obtained during desorption carried out with 0.1 M HCl. The peak of Fe is much smaller than the peak of Cu which is in agreement with the higher selectivity of the biomass for Cu. A comparison of the scales of the horizontal axes used in Figs 3 and 4 shows that for copper the desorption was approximately nine times faster than the process of the column saturation.

The capacity of an ion exchange resin, commonly expressed in milliequivalents of ions bound per gram of the resin, serves as a basis for preliminary design calculations concerning ion exchange processes. The capacity of the *Sargassum* biosorbent was previously reported to be approximately 2.3 meq/g (Fourest and Volesky, 1996; Kratochvil *et al.*, 1997). For single component systems, the capacity of an ion exchanger with respect to the given species is equal to the overall, i.e. the maximum, resin capacity. Owing to competitive sorption, however, the uptake of a species from a multicomponent mixture is lower than the uptake of the same species from a single component system. Figure 5 summarizes the effect of the increasing concentration of Fe^{2+} on the uptake of Cu by *Sargassum* biosorbent. The curves in Fig. 5, calculated using