BIOSORPTION OF Cu FROM FERRUGINOUS WASTEWATER BY ALGAL BIOMASS

DAVID KRATOCHVIL and BOHUMIL VOLESKY*
Department of Chemical Engineering, McGill University, 3480 University Street, Montreal, Que., Canada H3A 2B2

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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

<table>
<thead>
<tr>
<th>Symbol</th>
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<tr>
<td>A, B</td>
<td>divalent metal species</td>
</tr>
<tr>
<td>C(M)</td>
<td>concentration of metal M in the liquid (meq/l)</td>
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<tr>
<td>C(M)/Cd(M)</td>
<td>concentration of metal M in the feed to a flow-through column (meq/l)</td>
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<tr>
<td>C_o</td>
<td>total normality of the feed to a flow-through column (meq/l)</td>
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<tr>
<td>C(M)/Cd(M)</td>
<td>relative concentration in column effluent</td>
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<tr>
<td>DO</td>
<td>dissolved oxygen</td>
</tr>
<tr>
<td>F</td>
<td>volumetric flowrate (m(^3)/h)</td>
</tr>
<tr>
<td>K_{AB}</td>
<td>equilibrium ion exchange constant defined by equation 5</td>
</tr>
<tr>
<td>q(M)</td>
<td>equilibrium uptake of metal M by the biosorbent (meq/g)</td>
</tr>
<tr>
<td>Q</td>
<td>concentration of metal binding sites in the biosorbent (meq/g)</td>
</tr>
<tr>
<td>T</td>
<td>dimensionless time in the ECM model</td>
</tr>
<tr>
<td>t</td>
<td>time (h)</td>
</tr>
<tr>
<td>V_C</td>
<td>volume of the packed-bed (m(^3))</td>
</tr>
<tr>
<td>y_A</td>
<td>equilibrium equivalent fraction of species A in the liquid</td>
</tr>
<tr>
<td>j_A</td>
<td>equilibrium equivalent fraction of species B in the sorbent</td>
</tr>
<tr>
<td>\rho_b</td>
<td>biomass packing density (g/m(^3))</td>
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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 (Voilesky, 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 Voilesky, 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...
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 specification 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.

$$\text{Fe}^{2+} + 1/4\text{O}_2 + \text{H}^+ = \text{Fe}^{3+} + 1/2\text{H}_2\text{O}$$  

(1)

$$\text{Fe}^{3+} + 3\text{H}_2\text{O} = \text{Fe(OH)}_3(s) + 3\text{H}^+$$  

(2)

If the pH drops below 3, the ferric ions cease to precipitate and remain in water in partially hydrolyzed forms (Dudney 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 (Dudney 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):

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

(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 biosorbents, 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

$$\text{A}^{2+} + (\text{B} - \text{biomass}) \leftrightarrow \text{B}^{2+} + (\text{A} - \text{biomass})$$  

(4)

The corresponding equilibrium constant is defined as

$$K_{AB} = \frac{q_A C_B}{q_B C_A}$$  

(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

$$Q = q_A + q_B$$  

(6)

The total normality of the solution $C_0$ is given by

$$C_0 = C_A + C_B$$  

(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

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

(8)

where $k = 1/K_{AB}C_A$. 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

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

(9)

yielding equation (10) which represents the binary ion exchange isotherm for the system
\[ y_A = \frac{1}{1 + (x_B / K_{AB}y_A)} \] (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 preadsorption of 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:

\[ T = \frac{C_B F_t}{\rho_a Q V_C} \] (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. \( x_{B2} \), \( x_{C2} \), \( x_{B2} \) 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:

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

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 Helliferich (1967a,b).

**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 H₂SO₄ 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$_2$SO$_4$ 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$_2$SO$_4$ to pH 3.0 and 2.1, respectively. During the experiments, solutions were pumped from a 401 storage tank to the column through a 1.51 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 3100D). The concentration of Fe$^{2+}$ was measured according to the Penny-Knopp 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 (Dohrmann DC-80) by both combustion and UV-peroxysulfate methods. All samples were acidified with concentrated H$_2$SO$_4$ 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: $R^2 = 0.99$).

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 $K_{CuFe} = 2.04$ 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. 2. Binary ion exchange isotherms calculated by using equation 10: (x) A = Cu, B = Fe, $K_{AB} = 6.7$; (O) A = Fe, B = Ca, $K_{AB} = 0.3$. 
why 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 (Kratochvíl 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 (Hellferich, 1965), (b) the pretreatment of the biomass and (c) the number of completed sorption/desorption cycles, i.e. biomass aging (Kratochvíl et al., 1997).

Desorption of the metals deposited in the biosorbent is likely (Kratochvíl 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; Kratochvíl 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...
Fig. 5. Summary of Cu uptake reduction due to the presence of Fe$^{2+}$ Cu uptake as a % of Q: (O) C(Cu) = 0.25 meq/l; (—) C(Cu) = 1 meq/l; (x) C(Cu) = 4 meq/l.

Fig. 6. Breakthrough curves of Cu$^{2+}$ from a column receiving a feed containing 25 mg/l Cu$^{2+}$ and: (■) no Fe(III) SS; (○) 15 mg/l Fe(III) SS; (x) 40 mg/l Fe(III) SS; bed volume = 200 ml; flowrate = 3 cm/min.

equation (5), show the equilibrium uptake of Cu expressed as the fraction of the maximum Cu uptake plotted against the equilibrium concentration of Fe$^{2+}$ in the liquid at equilibrium Cu$^{2+}$ concentrations of 0.25, 1 and 4 meq/l (8, 33 and 120 mg/l). The range of Fe$^{2+}$ concentration on the horizontal axis, i.e. 0-12 meq/l (0-330 mg/l) in Fig. 5 is relatively broad and covers a large portion of industrial effluents (Dudeny et al., 1994; Gazza et al., 1996). It can be seen from Fig. 5 that with increasing concentration of Fe$^{2+}$, the Cu uptake initially drops rather sharply but subsequently tends to plateau at approximately 10, 40 and 70% of the maximum Cu uptake for C(Cu) = 0.25, 1 and 4 meq/l, respectively. The lower the Cu concentration in the liquid, the greater the overall reduction of Cu uptake caused by Fe$^{2+}$ and the lower the amount of Fe$^{2+}$ needed to decrease the Cu uptake by a fixed percentage.

As mentioned above, ferruginous wastewater with a relatively high level of DO and a pH > 3 is likely to contain most of the iron in the form of Fe(III) suspended solids (SS). The effect of the presence of Fe(III) SS on the performance of a flow-through biosorption column used to remove Cu from water is summarized in Figs 6-8. Figures 6 and 7 show that the biosorption column was effectively sorbing Cu from the feed while functioning as a filter for the Fe(III) solids at the SS level of 15 and 40 mg/l. Furthermore, Fig. 8 shows that the pressure drop build-up due to the retention of solids in the packed-bed was relatively slow, hence allowing the operation of the column to continue until the breakthrough of Cu. However, Fig. 6 shows that as the level of SS in the feed increased from 0 to 40 mg/l, the column cleaned lower number of bed volumes of water. This shortening of the column service time, represented in Fig. 6 by the shift of the Cu breakthroughs along the horizontal axis to the left, can be anticipated since the SS retained in the column decreased the porosity of the packed bed, thereby blocking access to a portion of the sorption sites in the biomass. The fact that the pressure drop across the column increased approximately linearly with time provides an indication that most of the solids penetrated deeply into the bed (Cleasby and Baumann, 1962). The values of

Fig. 7. Percentage removal of Fe(III) SS in a column: (O) 15 mg/l Fe(III) SS; (x) 40 mg/l Fe(III) SS; bed volume = 200 ml; flowrate = 3 cm/min.

Fig. 8. Pressure drop build-up across a column receiving a feed containing: (O) 15 mg/l Fe(III) SS; (x) 40 mg/l Fe(III) SS; bed volume = 200 ml; flowrate = 3 cm/min.
specific solid capture of 50 and 90 g·m⁻²·kPa⁻¹, calculated from the experimental results with SS levels of 15 and 40 mg/l and displayed in Fig. 6 through 8, compare well with the range of specific solid capture values of 57–114 g·m⁻²·kPa⁻¹ reported for granular media filters (U.S. EPA, 1975).

No change in Cu²⁺ concentration was detected in the stirred tank over the course of individual experiments. This is in agreement with data previously published by Gutzman and Langford (1993) predicting a negligible uptake of Cu by the hydrous ferric oxide at pH 4.5 and for the Fe/Cu molar ratios lower than 0.5 which were used in the present work.

Figure 9(a) and (b) display the concentration of TOC as it was measured in the column effluent during sorption and desorption experiments, respectively. TOC represents the organic material leaching from the biosorbent and thus can serve as an indicator of the chemical stability of the biosorbent. The fairly low average TOC levels of 4 mg/l during sorption and 30 mg/l during desorption shown in Fig. 9(a) and (b) indicate that the Sargassum biosorbent is relatively stable. The fact that more organic matter leaches from the algal biosorbent during desorption may be explained by a partial extraction of acid soluble components from the seaweed biosorbent when exposed to a relatively strong acid wash solution.

As long as all of the iron present in the water is in the form of either Fe(III) SS, or Fe²⁺, the oxidation of the biosorbent by Fe(III) is prevented. The reductive dissolution of Fe(III) SS by soluble organic matter leaching from the biosorbent may occur. However, the dissolution of the Fe(III) SS would not substantially interfere with Cu removal considering the time scale of one biosorption cycle and the fact that the dissolution according to equation (3) is known to be a very slow process (Deng and Stumm, 1993; Vile and Wieder, 1993).

CONCLUSIONS

The options for a biosorption process utilizing Sargassum biosorbent to remove and recover copper from ferrous water are summarized below for the two extreme cases of water containing only ferrous iron and water containing exclusively ferric iron.

Water with a low level of DO and all of the iron in ferrous (Fe²⁺) form

Using [C(Cu²⁻), C(Fe³⁺)] coordinates, the regions of high, intermediate, and negligible interference of Fe³⁺ in the sorption of Cu²⁻ were constructed in Fig. 10. In the regions of high and negligible interference, iron lowers the uptake of copper by more than 40% and by less than 10%, respectively, as compared to the copper uptake from water containing only Cu²⁻. The borders between the regions in Fig. 10 were calculated using equation (8) and fixed values of q(Cu)/Q of 0.6 and 0.9, respectively, and are represented by straight lines as a result of the linear relationship between Ce and Cu which can be written as

\[
C_{Fe} = C_{Cu} + \left( \frac{q_{Cu}}{Q} - 1 \right) K_{CeFe}
\]  

(15)

Equation (15) can be obtained by rearranging equation (8) for A = Cu and B = Fe. It is clear that the removal/recovery of Cu from ferrous water by biosorption can be considered effective only if the metal content of water falls into the ranges of either low or intermediate interference.

Water containing only ferric iron in the form of Fe(III) suspended solids

It is known that the uptake of copper by Sargassum biomass increases with the increasing pH of wastewater. However, at pH > 5, copper may start precipitating as Cu(OH)₂ depending on the concentration of Cu²⁺. Furthermore, according to Gutzman and Langford (1993), at pH > 5.5 the Cu²⁺ ions have much higher tendency to sorb onto Fe(III) SS than at a lower pH. It follows that the optimum pH for the removal of Cu²⁺ by biosorption onto Sargassum lies in the range of pH 4–5.

Fig. 9. Leaching of organic matter from Sargassum biosorbent packed in a column: (a) TOC in column effluent during sorption; (b) TOC in column effluent during desorption with 0.1 M HCl; bed volume = 200 ml; flow rate = 3 cm/min.
Figure 11 summarizes the interference of Fe(III) SS in the removal of Cu\(^{2+}\) by biosorption at pH 4.5. Water containing less than 40 mg/l Fe(III) SS may be directly fed into biosorption columns. If the level of SS in the water exceeds 40 mg/l, a partial removal of SS in a pond and/or a clarifier is necessary prior to biosorption of copper in columns. As mentioned above, a portion of the overall Cu content may sorb on the Fe(III) precipitate during settling, depending on the pH and Cu:Fe molar ratio. The dashed lines indicating the percentage of the overall Cu content sorbing onto Fe(III) SS in Fig. 11 were calculated from data previously published by Gutzman and Langford (1993). It should be noted that these dashed lines are straight due to the fact that at a fixed molar ratio of Fe:Cu in an effluent, the fraction of the overall Cu sorbing onto Fe(III) SS is constant (Gutzman and Langford, 1993). Although the knowledge of the equilibrium exchange constant \(K_{Cu/Fe}\) allows prediction of the uptake of copper by the biomass in the system containing Fe\(^{2+}\), Fe(III) and Cu\(^{2+}\), a 3D plot would be necessary to show the dependence of the copper uptake by Sargassum as a function of the waste-water composition. The analysis of 3D plots related to biosorption data was presented earlier by Figueira et al. (1997) and is beyond the scope of this work.

REFERENCES


