



## Copper biosorption on immobilized seaweed biomass: Column breakthrough characteristics

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### Abstract

The biosorption of copper by the brown seaweed *Sargassum baccularia*, immobilized onto polyvinyl alcohol (PVA) gel beads, was investigated with fixed-bed experiments. Laboratory-scale column tests were performed to determine breakthrough curves with varying flow rates and feed concentrations. A theoretical fixed-bed model, known as the Bohart-Adams equation, was evaluated in simulating the experimental breakthrough curves. The Bohart-Adams model qualitatively predicted the breakthrough trends. PVA-immobilized seaweed biomass beads were amenable to efficient regeneration with aqueous solution containing the chelating agent ethylenediaminetetraacetic acid (EDTA). The biosorbent retained most of its original uptake capacity over three cycles of use. The excellent reusability of the biosorbent could lead to the development of a viable metal remediation technology.

**Key words:** adsorption; biosorption; fixed bed; immobilized algae; polyvinyl alcohol

### Introduction

Improper treatment and disposal of metal-contaminated wastewaters raise concerns for soil and water contamination. Conventional treatment methods such as chemical precipitation and reverse osmosis become inefficient or expensive when the metals are present in trace quantities. Biosorption—a process that relies on the passive uptake of metal ions by inactivated biomass of microorganisms or plants—appears to be one of the most promising treatment techniques available for such situations. The basis of metal biosorption has been attributed to the existence of a myriad of surface ligands like carboxyl, sulfate, amino, and hydroxyl moieties. These ligands differ in their affinity and specificity for metal binding. As a result, biosorption is a non-specific process. A given biomass will bind more than one metal ion when exposed to solutions containing several metal ions.

One form of biomass that has shown impressive metal binding properties is marine macroalgae, commonly referred to as seaweeds (Mehta and Gaur, 2005). Seaweeds are a widely available source of low-cost biomass as over two million tonnes are either harvested from the oceans or cultured annually for food or phycocolloid production (Zemke-White and Ohno, 1999). Various species of seaweeds have been tested in the laboratory for removal of a range of toxic metal ions (Feng and Aldrich, 2004; Hashim and Chu, 2004; Herrero *et al.*, 2005; Luo *et al.*,

2006; Park *et al.*, 2005; Suzuki *et al.*, 2005; Xian *et al.*, 2006). For industrial-scale operation biosorption can be easily implemented using the well-established activated carbon fixed-bed system since design procedures as well as process equipment for this type of operation are readily available (Cooney, 1999). It is therefore desirable to develop biosorption processes for metal removal based on the fixed-bed configuration.

Although seaweed biomass in its native form has been used in fixed-bed studies (Cossich *et al.*, 2004; da Silva *et al.*, 2002; Vijayaraghavan *et al.*, 2005; Zeroual *et al.*, 2003), the biomass in general has a tendency to disintegrate and swell, causing operational problems such as clogging and pressure drop fluctuations. To be of practical use, seaweed biomass can be immobilized onto porous solids to increase its stability and mechanical strength. Many natural and synthetic polymers have been used for biomass immobilization. In the case of seaweed biomass immobilization, polyvinyl alcohol (Chu and Hashim, 2001) and polyurethane (Alhakawati and Banks, 2004; Zhang and Banks, 2006) have been successfully used. Polyvinyl alcohol (PVA) is a type of synthetic polymer that is readily available, cheap, and possesses excellent attrition resistance properties. The broad objective of this study is to present a series of laboratory investigations carried out to evaluate the pertinent properties of PVA-immobilized seaweed biomass for its use in fixed-bed systems for copper removal. Theoretical analysis using a simplistic fixed-bed model is also included in the study.

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## 1 Materials and methods

### 1.1 Materials

Samples of the brown seaweed *Sargassum baccularia* were collected from the west coast of Peninsular Malaysia. The biomass was washed thoroughly to remove adhering sand and dried to a constant weight. It was then ground and sieved to a size range of 250–500  $\mu\text{m}$ . Polyvinyl alcohol (MW = 72000), disodium salt of ethylenediaminetetraacetic acid (EDTA), copper nitrate salt, boric acid, and sodium phosphate were obtained from Fluka, Switzerland.

### 1.2 Biomass immobilization

An immobilization method published in the literature (Chen and Lin, 1994) was adopted in this work to immobilize seaweed particles onto PVA beads. Seaweed particles were mixed with an aqueous PVA solution (15%, w/v) to produce a mixture with a solid-to-liquid ratio of approximately 150 g/L. The resulting mixture was transferred to a syringe and released into a gently stirred saturated boric acid solution to form spherical beads. The beads were then transferred to a sodium phosphate solution for hardening, followed by washing with distilled water to remove residual chemicals.

### 1.3 Column experiments

PVA-immobilized biomass beads were packed in a glass column with a diameter of 1.6 cm to a height of 10 cm. The temperature of the water-jacketed column was maintained at 25°C. Distilled water adjusted to pH 5 was pumped through the column using a liquid chromatography pump (Perkin Elmer, USA) to condition the beads. Three column tests were performed to determine breakthrough curves at different flow rates (1 or 1.5 ml/min) and feed concentrations (20 or 40 mg/L). A feed solution of known copper concentration adjusted to pH 5 was pumped through the column at a known flow rate. Samples were collected at the column outlet at fixed time intervals and analyzed for copper concentration using an inductively coupled plasma atomic emission spectrophotometer (ICP-AES) (ICP 2000, Baird, USA).

In the experiments consisting of multiple biosorption-desorption cycles, the biosorbent column was first loaded with copper. Upon saturation, the feed flow was replaced

with a distilled water flow to flush out any unbound copper from the column. Aqueous solution containing 2 mmol/L EDTA was then pumped through the column to elute the bound copper from the beads. Samples were collected at the column outlet at fixed time intervals and analyzed for copper by the ICP-AES. At the end of the elution step, distilled water adjusted to pH 5 was pumped into the column to recondition the beads and to displace any remaining EDTA solution that might interfere with the next cycle of copper loading. The biosorbent column, now free of copper and EDTA, was ready for reuse. The above experimental procedure constituted one cycle of copper loading and elution. Three consecutive cycles were conducted to assess the performance of PVA-immobilized biomass beads under continuous flow conditions.

## 2 Results and discussion

Fig.1a shows the experimental breakthrough curves (points) for a feed containing 20 mg/L copper obtained at two different flow rates, while Fig.1b displays those for two different feed concentrations measured at a flow rate of 1 ml/min. Breakthrough curves calculated from a theoretical model are also included in Fig.1 (lines) and these are discussed later. Fig.1a shows that when the flow rate increased from 1 to 1.5 ml/min the time required for complete column saturation decreased from 900 min to about 600 min. The breakthrough curve obtained at the higher flow rate shows a much shorter clear period (i.e., undetectable effluent copper concentration) before the breakthrough point (the point that copper was first detected in column effluent) and a much sharper shape. Increasing the feed concentration produced a similar trend, as shown in Fig.1b; the breakthrough curve shifted towards the origin with increasing feed concentration. The slope of the breakthrough curve for the 20 mg/L feed is noticeably less sharp than that of the breakthrough curve for the 40 mg/L feed.

Mathematical models are useful for understanding fixed-bed column dynamics and for design and optimization studies since they help reduce time-consuming and repetitive experiments. Various fixed-bed models of varying complexity have been used to study the dynamics of immobilized biosorbent systems (Borba *et al.*, 2006; Cosich *et al.*, 2004; da Silva *et al.*, 2002; Hatzikioseyian *et al.*,

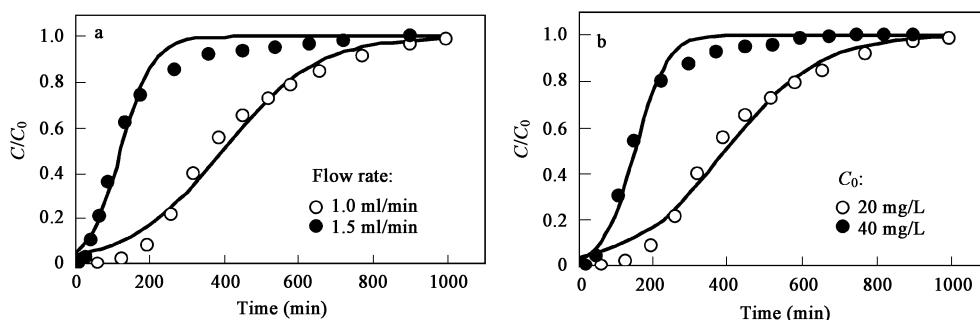


Fig. 1 Effect of flow rate on breakthrough curves at feed concentration of 20 mg/L (a) and effect of feed concentration ( $C_0$ ) on breakthrough curves at flow rate of 1 ml/min (b). Points are experimental; curves are best-fitting model simulations obtained from Eq.(4).

2001). Although such models are useful for a fundamental understanding of the dynamics of fixed-bed columns, their practical utility is rather limited owing to the complicated solution methods. On the other hand, simplified models are useful when it is desired to develop a practical tool that can capture quantitatively the effects of main system variables on the column dynamics. In this work, the ability of a relatively simple fixed-bed model, known as the Bohart-Adams equation (Bohart and Adams, 1920), to describe the breakthrough behavior of PVA-immobilized biomass beads was examined. The development of the Bohart-Adams model follows.

We consider an isothermal column packed with a biosorbent through which a fluid containing a metal ion flows with constant linear velocity. The differential mass balance for the column is given by:

$$v \frac{\partial C}{\partial z} + \frac{\partial C}{\partial t} + \left( \frac{1 - \varepsilon}{\varepsilon} \right) \frac{\partial q}{\partial t} = D_L \frac{\partial^2 C}{\partial z^2} \quad (1)$$

where,  $C$  is the fluid phase metal concentration,  $q$  is the metal concentration in the biosorbent averaged over the biosorbent volume,  $v$  is the interstitial velocity,  $D_L$  is the axial dispersion coefficient,  $\varepsilon$  is the column void fraction,  $z$  is the axial coordinate with origin at the column inlet, and  $t$  represents time. The initial and boundary conditions for the column initially free of metal and subjected to a step change in metal concentration at the column inlet at time zero are given by:

$$t = 0, C = q = 0$$

$$z = 0, \frac{D_L}{v} \frac{\partial C}{\partial z} = C - C_0$$

$$z = L, \frac{\partial C}{\partial z} = 0$$

where,  $C_0$  is the metal concentration of the feed solution and  $L$  is the column length. The term  $\partial q/\partial t$  in Eq.(1) represents the local rate of adsorption between the fluid and biosorbent phases. Various dynamic models have been derived which differ mainly in the choice of kinetic rate expression. The Bohart-Adams model assumes that adsorption can be described by a quasi-chemical kinetic rate expression:

$$\frac{\partial q}{\partial t} = bC(q_s - q) \quad (2)$$

where,  $q_s$  is the saturation capacity of the biosorbent and  $b$  is a rate constant. Neglecting axial dispersion, the analytical solution to Eqs.(1) and (2), first obtained by Bohart and Adams (1920), is given by:

$$\frac{C}{C_0} = \frac{\exp\left(bC_0\left(t - \frac{L}{v}\right)\right)}{\exp\left(bC_0\left(t - \frac{L}{v}\right)\right) + \exp\left(\frac{bq_s L}{v}\left(\frac{1-\varepsilon}{\varepsilon}\right)\right) - 1} \quad (3)$$

A useful approximation to Eq.(3) is to assume  $t \gg L/v$  and to disregard the “1” term in the denominator (Cooney, 1999). These two simplifications allow us to express Eq.(3) as:

$$\frac{C}{C_0} = \frac{1}{1 + \exp\left(b\left(a\frac{L}{u} - C_0 t\right)\right)} \quad (4)$$

where,  $u$  is the superficial velocity ( $u = \varepsilon v$ ) and  $a$  is the saturation capacity of the biosorbent per unit volume of the packed bed ( $a = q_s(1 - \varepsilon)$ ). Upon rearrangement, Eq.(4) becomes:

$$t = a \frac{L}{uC_0} - \frac{1}{b} \frac{\ln\left(\frac{C_0}{C} - 1\right)}{C_0} \quad (5)$$

According to Eq.(5), plotting experimental data in terms of  $t$  versus  $\ln(C_0/C-1)/C_0$  should yield straight lines and the two parameters  $a$  and  $b$  can be estimated from the corresponding intercepts and slopes, respectively. Note that the Bohart-Adams model is sometimes inadvertently referred to as the Thomas model in the biosorption literature. Nonetheless, the Bohart-Adams model is closely related to the Thomas model and can be regarded as a limiting form of the latter (Ruthven, 1984).

Fig.2 displays the breakthrough data of Figs.1a and 1b plotted in terms of Eq.(5). In all cases, a linear relationship between  $t$  and  $\ln(C_0/C-1)/C_0$  is not found, indicating that the experimental results do not conform to the linearized Bohart-Adams model. The implication is that  $a$  and  $b$  cannot be estimated from these nonlinear curves.

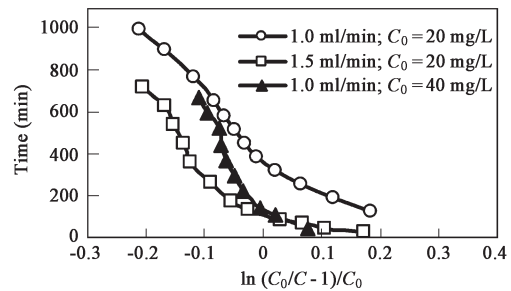


Fig. 2 Experimental breakthrough data plotted according to Eq.(5).

An alternative method of estimating  $a$  and  $b$  is to fit Eq.(4) directly to the breakthrough data of Figs.1a and 1b by a nonlinear least-squares fit. The values of  $a$  and  $b$  obtained using this approach are tabulated in Table 1. Calculated curves using these values for  $a$  and  $b$  are shown as lines in Figs.1a and 1b, in comparison with the experimental data. Overall, the agreement between the experimental curves and calculated ones is approximate. In particular, the model overestimated the sharpness of the leading and trailing edges of the experimental breakthrough curves.

Table 1 Best-fit values of Bohart-Adams parameters obtained by fitting Eq.(4) to experimental breakthrough curves

| Flow rate (ml/min) | $C_0$ (mg/L) | Bohart-Adams parameters |                      |
|--------------------|--------------|-------------------------|----------------------|
|                    |              | $a$ (mg/L)              | $b$ (L/(mg·min))     |
| 1.0                | 20           | 393.64                  | $0.4 \times 10^{-3}$ |
| 1.5                | 20           | 184.90                  | $1.2 \times 10^{-3}$ |
| 1.0                | 40           | 302.48                  | $0.5 \times 10^{-3}$ |

The discrepancies between the measured and calculated breakthrough curves can be ascribed to the approximations inherent in using the simplistic Bohart-Adams model, which is capable of generating symmetrical, sigmoidal

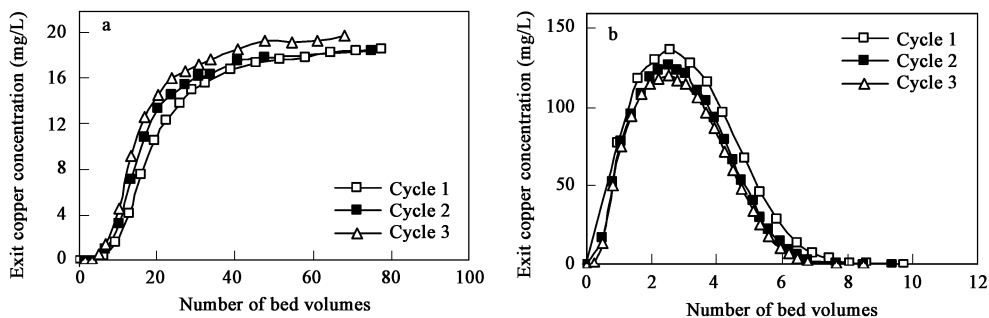


Fig. 3 Multiple-cycle breakthrough curves with PVA-immobilized *Sargassum* biosorbent at: feed flow rate = 1 ml/min;  $C_0 = 20$  mg/L (a); eluant flow rate = 1 ml/min; EDTA in eluant = 2 mmol/L (b).

breakthrough curves. The nonlinear plots in Fig.2 indicate that the experimental breakthrough curves reported here are asymmetrical. The broadness of the trailing edge of the breakthrough curves could perhaps result from slow intraparticle diffusion within the pores of the biosorbent beads. Copper must first diffuse into the porous beads before interacting with the functional groups of *Sargassum* biomass. The “tailing” of a breakthrough curve (i.e., a slow approach of  $C/C_0$  towards 1) is commonly observed in liquid phase adsorption where intraparticle diffusion is the dominant mass transfer process (Cooney, 1991). The Bohart-Adams model does not explicitly account for the phenomenon of intraparticle diffusion as it uses a quasi-chemical kinetic rate expression to describe mass transfer.

To be viable for practical application, immobilized biomass should retain its metal uptake property over multiple cycles of use. In this study, PVA-immobilized *Sargassum* biomass beads were used for copper biosorption and desorption over three cycles of fixed-bed operation. Each cycle essentially consisted of loading with a copper solution of 20 mg/L at a pH of 5 and desorption with 2 mmol/L EDTA. The resulting breakthrough and elution profiles for each cycle are shown in Figs.3a and 3b, respectively. In these figures the effluent copper concentration is plotted against the number of bed volumes, which is defined here as the ratio of the volume of treated solution to the volume of the fixed-bed. Fig.3a shows that when virgin immobilized biomass was first exposed to copper solution in the first cycle, copper breakthrough was observed at approximately 6 bed volumes. The breakthrough was essentially complete at about 50 bed volumes. In the second and third cycles the breakthrough curves shifted slightly towards the origin, indicating slight reductions in copper uptake which may be attributed to the adverse effect of EDTA on some of the copper binding sites. As EDTA is a strong metal chelating agent, it might have altered the configuration of some binding sites following stripping of the adsorbed copper by EDTA in the first cycle. This would have caused the slight reductions in copper uptake observed in subsequent cycles. Another probable explanation is that the relatively bulky EDTA molecule was not able to approach some of the copper binding sites owing to steric hindrance.

In each cycle, aqueous solution containing 2 mmol/L EDTA was pumped through the column to elute the

adsorbed copper. The resulting elution profiles for the three cycles are shown in Fig.3b. In the first cycle the effluent copper concentration increased rapidly after a short period of time to a maximum of about 136 mg/L, followed by a rapid decline in the effluent copper concentration that eventually reached zero at about 8 bed volumes. Similar profiles were observed for the second and third cycles but with slightly lower maximum concentrations. Estimations of the amount of copper loaded and the amount of copper eluted in each cycle from the respective breakthrough and elution curves indicate that almost complete recovery of the bound copper was readily achieved in each case. It is in principle possible to produce a highly concentrated, low volume effluent by optimizing the elution conditions such as the EDTA concentration and flow rate. The biosorption column packed with PVA-immobilized *Sargassum* biosorbent can thus be considered as an efficient metal concentration process that can be used to treat large volumes of wastewater contaminated with trace amounts of copper.

### 3 Conclusions

This work has demonstrated that seaweed biomass immobilized in PVA gel was compatible with fixed-bed column operation for copper removal. A positive aspect of this biosorbent was that it exhibited favorable regeneration conditions, with nearly complete regeneration achieved with aqueous solution containing EDTA. The metal uptake property of the biosorbent remained practically unaltered during three successive cycles of biosorption-desorption. The Bohart-Adams model was used to describe breakthrough profiles obtained at different flow rates and feed concentrations. Calculated breakthrough curves of the model were in approximate agreement with the experimental ones. It was established that the column behavior of this biosorbent was not entirely predictable on the basis of the simplistic Bohart-Adams model. A more detailed analysis using mass transfer models will be the subject of future communications.

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