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Continuous Packed Bed Biosorption of Copper by Immobilized Seaweed Biomass

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ABSTRACT

The biosorption of copper by inactivated biomass of the brown seaweed *Sargassum baccularia*, immobilized onto polyvinyl alcohol (PVA) gel beads, was investigated using a laboratory-scale packed bed column. Continuous-flow column tests were performed to determine breakthrough curves at two different column lengths. In both cases, a very broad trailing edge of the breakthrough curve was observed, indicating the presence of intraparticle diffusion resistance within the biomass beads. Such asymmetric breakthrough curves could not be described by a simplified two parameter packed bed model. A positive aspect of the PVA-immobilized biomass was that its copper uptake capacity remained essentially unaltered over two consecutive cycles of adsorption-desorption. The biomass beads could be regenerated for reuse with an aqueous solution containing 4mM ethylenediaminetetraacetic acid. The robustness and stability of the immobilized biomass beads could lead to the development of an efficient and cost-effective bioremediation technology for the removal and recovery of toxic metals from aqueous solutions.

Keywords: Algae; Biosorption; Fixed bed; Immobilized biomass; Seaweeds

1. INTRODUCTION

In recent years increasing concern about the effect of toxic metals on plant and animal life has led to the implementation of more stringent environmental regulations in many parts of the world for industrial and mining operations that discharge metal-bearing effluents. As a result, highly efficient metal removal technologies are needed to reduce the metal concentrations in wastewater to acceptable regulatory standards. Biosorption is one such technology that is gaining attention among environmental researchers.

Biosorption exploits the ability of microbial and plant biomass to sequester heavy metal ions from aqueous solutions by physicochemical mechanisms. Numerous species of nonliving biomass have been screened and studied extensively in the last decade with the aim of identifying highly efficient and selective metal removal biosorbents. For example, various species of seaweeds have been shown to possess impressive binding capacities for a range of toxic metal ions (Seki and Suzuki, 1998; Zhou *et al.*, 1998; Kim *et al.*, 1999; Malik *et al.*, 1999; Sanchez *et al.*, 1999; Yu *et al.*, 1999; Davis *et al.*, 2000; Esteves *et al.*, 2000; Hamdy, 2000; Stirk and van Staden, 2000; Cabatingan *et al.*, 2001; Romero-Gonzalez *et al.*, 2001; Lee *et al.*, 2002). Since design procedures as well as process equipment for conventional activated carbon packed bed columns are readily available (Cooney, 1999), biosorption for full-scale applications can in principle be implemented using the packed bed configuration. It is therefore desirable to develop biosorption processes for metal removal based on the packed bed configuration.

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Although seaweed biomass in its native form has been used in packed bed studies (Kratochvil *et al.*, 1995; Costa and Franca, 1996; Yu and Kaewsarn, 1999), 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, the biomass can be immobilized on porous solids to increase its mechanical strength (Chu and Hashim, 2001). The objective of this paper is to investigate the column performance of the brown seaweed *Sargassum baccularia* immobilized in polyvinyl alcohol (PVA) gel beads using copper as a model metal ion. PVA is a type of synthetic polymer that is readily available, cheap, and possesses strong mechanical strength and durability.

2. MATERIALS AND METHODS

Samples of *S. baccularia* were collected from the west coast of Peninsular Malaysia. The biomass was washed and dried to a constant weight. It was then ground and sieved to a size range of 250-500μm. The resulting seaweed biomass particles were mixed with an aqueous solution of PVA (15% w/v) to produce a mixture with a solid-to-liquid ratio of approximately 150g/l. The mixture was transferred to a syringe and released into a gently stirred saturated boric acid solution to form spherical beads of 0.35cm in diameter. The beads were then placed in a sodium phosphate solution (1.0M) for hardening, followed by washing with distilled water to remove residual chemicals (Chen and Lin, 1994). A scanning electron microscope (LEICA S440) was used to obtain microscopic images of immobilized biomass beads.

PVA-immobilized biomass beads were packed in a glass column with a diameter of 1.6cm. Two continuous-flow column tests were performed to determine breakthrough curves at different bed lengths (11 and 13cm). A copper solution of 20mg/l adjusted to a pH of 6 was pumped through the column at a flow rate of 1ml/min using a liquid chromatography pump (Perkin Elmer, USA). Samples were collected at the column outlet at fixed time intervals and analyzed for copper concentration using an inductively coupled plasma atomic emission spectrophotometer (Baird, USA).

In the experiments comprising two consecutive cycles of adsorption-desorption to assess the performance of immobilized biomass beads under continuous flow conditions, 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. An aqueous solution containing 4mM ethylenediaminetetraacetic acid (EDTA), a strong metal chelating agent, 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. At the end of the elution step, distilled water adjusted to a pH of 6 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 biosorption column, now free of copper and EDTA, was ready for reuse. The above experimental procedures constituted one cycle of copper loading and elution.

3. RESULTS AND DISCUSSION

Figure 1 shows the experimental breakthrough curves for a feed containing 20mg/l copper obtained at two different bed lengths (symbols). Theoretical breakthrough curves calculated from a mathematical model are also included in Figure 1 (lines) and these are discussed later. The results are plotted as the ratio of the effluent concentration (C_e) to the influent concentration (C_i) versus time. The shape of the breakthrough profile is determined by the shape of the equilibrium isotherm and is influenced by the individual transport processes taking place in the flowing liquid phase as well as in the immobilized biomass beads. Figure 1 shows that the breakthrough curve shifted towards the origin with increasing bed length. For short times (2-3h) copper in the feed was taken up completely by the column. As expected, the curve for the shorter column showed a shorter clear period (i.e., undetectable effluent copper concentration).

In both cases, a very broad trailing edge of the breakthrough curve was observed and the time required for complete saturation of the column was in excess of 35h.

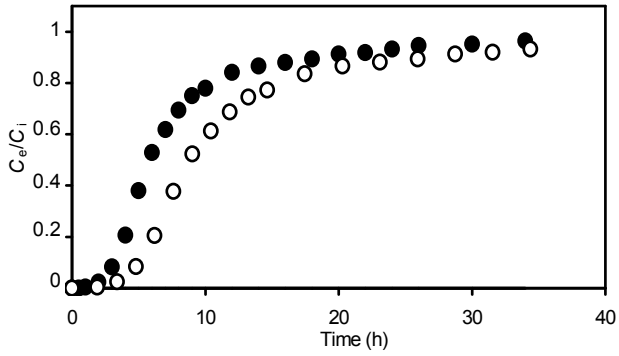

Figure 1. Effect of bed length on breakthrough curves on PVA-immobilized seaweed biomass. Feed concentration = 20mg/l. Flow rate = 1ml/min. Open circles, experimental, bed length = 13cm; closed circles, experimental, bed length = 11cm; lines, model fits obtained from Eq. (1)

Mathematical models are useful for design and optimization studies since they help reduce time-consuming and repetitive experiments. An excellent summary of theoretical models for predicting breakthrough curves of columns packed with spherical adsorbents has been given by Ruthven (1984) and several of these models adapted for the design of activated carbon packed bed adsorbers for wastewater treatment are well covered in the recent book of Cooney (1999). In the general case a mechanistic model considers axial dispersion in the direction of the liquid flow, film diffusion resistance, intraparticle diffusion resistance which may include both pore and surface diffusion, and sorption kinetics at the adsorbent surface. Because of the nonlinearity associated with equilibrium expressions, a full solution of the resulting set of partial differential equations requires complicated numerical solution.

Because of the mathematical complexity and difficulty in determining some of the parameters employed in a full mechanistic model, simplified modeling approaches have been used by a number of investigators. The most commonly used simplification avoids the complexity of solving the partial differential equation for intraparticle diffusion by using the approximation of a linear driving force model. Another common simplification involves the assumption of local equilibrium which eliminates the need to consider the kinetics of adsorption. Trujillo *et al.* (1991) used a simplified packed bed model that considers plug flow of the liquid phase and a linearized mass transfer rate expression to model the breakthrough curves for a multimetal solution obtained with a column packed with immobilized sphagnum peat moss. Hatzikioseyian *et al.* (2000) applied a simplified packed bed model based on the concept of rapid local equilibrium to simulate experimental breakthrough curves selected from the biosorption literature. Mass transfer resistances in the liquid and solid phases and other rate processes were lumped into an apparent overall dispersion coefficient. In general, the above approaches require a numerical solution in cases where the equilibrium isotherm is nonlinear.

In this work we tested the capability of a relatively simple mathematical model to describe the experimental breakthrough profiles. The model with two adjustable parameters is given by (Belter *et al.*, 1988):

$$\frac{C_e}{C_i} = \frac{1}{2}\left(1 + \mathrm{erf}\left[\frac{t - t_a}{\sqrt{2}\sigma t_a}\right]\right) \qquad (1)$$

where erf[*x*] is the error function of *x*, *t* is the column residence time, t_a is the time at which the effluent concentration is half the influent concentration, and σ represents the standard deviation which is a measure of the slope of the breakthrough curve. Eq. (1) has been used to simulate the breakthrough curves for copper biosorption on polyvinyl formal-immobilized *Rhizopus arrhizus*

and native *Mucor miehei* (Brady *et al.*, 1999). The model parameters t_a and σ were estimated by fitting Eq. (1) to the experimental breakthrough data of Figure 1 using a nonlinear least-squares regression program based on a combination of Gauss-Newton and Levenberg-Marquardt methods. The fitted values of t_a and σ and the correlation coefficient r^2 are listed in Table 1. Breakthrough curves calculated using these best fit values are shown as lines in Figure 1, in comparison with the experimental data. It can be seen from Figure 1 that the agreement between experimental curves and calculated ones was approximate. In particular, the model overestimated the sharpness of the leading and trailing edges of the experimental curves. In addition, the model predicted a nonzero effluent concentration at t = 0 which contradicts real conditions.

Table 1.
Best fit values of t_a and σ obtained by fitting Eq. (1) to the entire experimental breakthrough profiles

Bed length (cm)	t_a (h)	σ	r^2
11	6.51	0.53	0.962
13	9.80	0.51	0.953

The discrepancy between measured and calculated curves can be ascribed to the approximations inherent in using simplistic packed bed models such as Eq. (1). Such models are in general capable of simulating only symmetric breakthrough curves. The experimental breakthrough curves of this study exhibited an asymmetric shape; a short leading edge followed by a very gradual approach to the feed concentration at the latter stage of the breakthrough. The broadness of the trailing edge was most likely due to slow intraparticle diffusion within the pores of the immobilized biomass beads. Figure 2 shows a scanning electron micrograph of the porous surface of a PVA-immobilized biomass bead. Copper ions must first diffuse into the porous bead before sequestration of the metal ion by seaweed biomass could take place. According to Cooney (1991), the 'tailing' of a breakthrough curve (i.e., a slow approach of C_e/C_i towards 1) is commonly observed in liquid phase adsorption where intraparticle diffusion is the rate-limiting transport process.

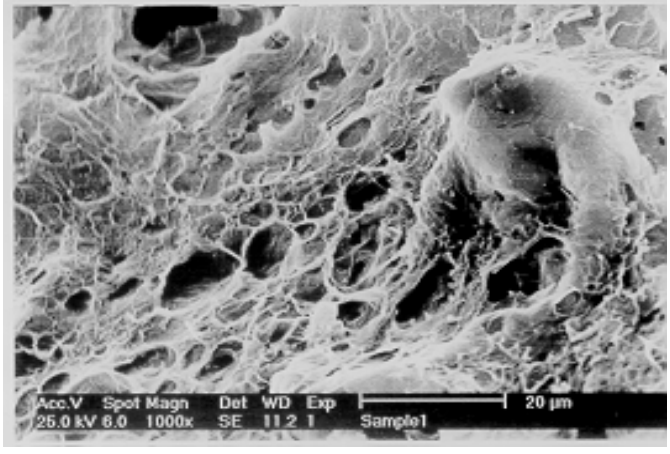

Figure 2. Scanning electron micrograph of the outer surface of an immobilized seaweed biomass bead

One way to improve the modeling capability of Eq. (1) is to omit the trailing edge of the breakthrough curve in the curve fitting process. Such a modeling approach could have practical benefits because it is often not necessary to model the entire breakthrough curve. In single column operations it is normal practice to terminate the influent flow at the breakthrough time at which the effluent concentration reaches a specified C_e/C_i value. This value is of course very small in order to meet regulatory standards for metal discharge. It is therefore of practical interest to simulate the initial stage of the breakthrough curve. Figure 3 shows the fitting of Eq. (1) to the experimental breakthrough curves using data at $C_e/C_i < 0.6$. The best fit t_a and σ

values along with the r^2 values are listed in Table 2. It is obvious that the calculated breakthrough curves were in excellent agreement with the experimental profiles. Such close agreement suggests that the simplified two parameter model can still be a practical tool that is accurate for the modeling of packed bed biosorption columns.

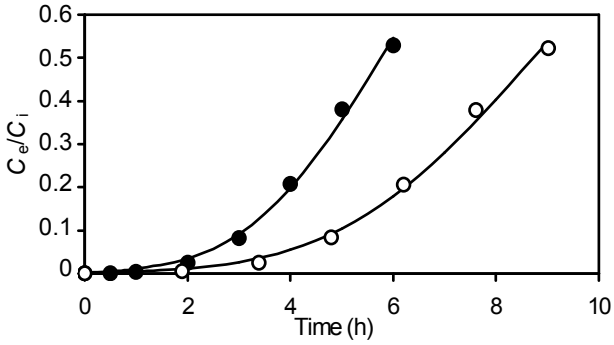

Figure 3. Comparison between experimental and calculated breakthrough curves for C_e/C_i <0.6. Open circles, experimental, bed length = 13cm; closed circles, experimental, bed length = 11cm; Lines, model fits obtained from Eq. (1)

Table 2.
Best fit values of t_a and σ obtained by fitting Eq. (1) to the experimental breakthrough profiles using data at $C_e/C_i < 0.6$

Bed length (cm)	t_a (h)	σ	r^2
11	5.76	0.36	0.996
13	8.73	0.34	0.995

To be viable for practical applications, immobilized biomass should retain its metal uptake capability over multiple cycles of use. In this study the performance of PVA-immobilized seaweed biomass was assessed over two consecutive cycles of copper loading and elution. Each cycle consisted of a loading step using a copper solution of 20mg/l and an elution step using an aqueous solution containing 4mM EDTA. The resulting breakthrough and elution profiles for each cycle are shown in Figures 4 and 5, respectively. Figure 4 shows that the two breakthrough curves are of similar shape, indicating that the metal uptake capacity of the immobilized biomass remained essentially unaltered over two adsorption-desorption cycles. Almost identical elution profiles were obtained for the two cycles, as shown in Figure 5. The effluent copper concentration increased rapidly after a short period of time, reaching a maximum of about 270mg/l, followed by a rapid decline in the effluent copper concentration. The whole elution process could be completed within 2.5h. The amounts of copper loaded and eluted in each cycle estimated from the respective breakthrough and elution curves indicate that almost complete recovery of the bound copper was readily achieved in each case.

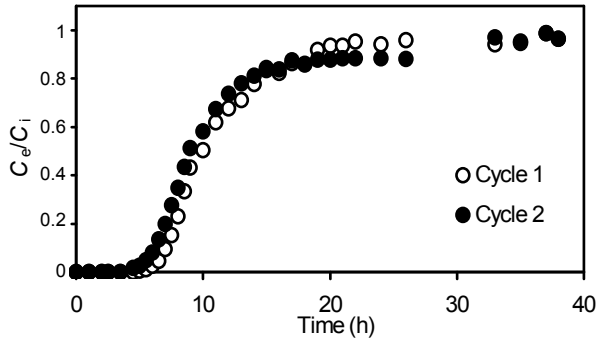

Figure 4. Multiple-cycle breakthrough curves. Feed concentration = 20 mg/l. Feed flow rate = 1 ml/min. Bed length = 13cm

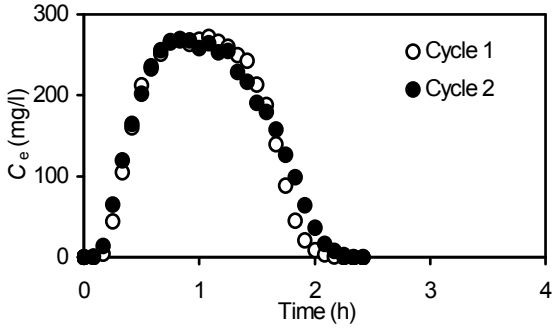

Figure 5. Multiple-cycle elution profiles. EDTA concentration in eluant = 4mM. Eluant flow rate = 1ml/min. Bed length =13cm

4. CONCLUSIONS

This work demonstrated that nonliving seaweed biomass immobilized in PVA gel beads could be used in a packed bed column for the removal and recovery of copper from aqueous solution. The continuous-flow column studies demonstrated the robustness of the immobilized biomass beads in repeated loading/elution cycles. The biomass beads could be regenerated with an aqueous solution containing 4mM EDTA. It was established that the dynamic behavior of the biosorption column was not entirely predictable on the basis of a simplified two parameter packed bed model. This was largely due to the fact that the two parameter model is only capable of simulating symmetric breakthrough curves. The breakthrough curves obtained in this study exhibited a very broad trailing edge due to slow intraparticle diffusion within the pores of the PVA-immobilized biomass beads. A more detailed analysis using mechanistic models will be the subject of a future communication.

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