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Efficiency of copper removal by *Sargassum sinicola* in batch and continuous systems

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Abstract The efficiency of batch and continuous systems of copper removal by *Sargassum sinicola* was studied. The effects of flow rate, initial metal concentration, and bed density on the capacity of the continuous system were also recorded. In batch systems, the maximum biosorption capacity was calculated as 49.63±0.88 mg g^{-1}; in the continuous system, under the following conditions: flow rate of 10 mL min^{-1}, initial solution of 200 mg Cu L^{-1}, bed density of 150 g L^{-1}, and higher copper removal of 62.39±1.91 mg g^{-1} was achieved. The Thomas model can be used to predict the breakthrough curves, but it underestimated breakthrough time.

Keywords Batch · Continuous · Copper · Removal · *Sargassum*

Introduction

Elevated concentrations of metals and metalloids in aqueous systems are increasingly recognized as a health hazard. Effluents from copper mining are a source of this metal which, depending on the final concentration in food or water, acts as an essential micronutrient or as a poison to living organisms (Da Silva et al. 2002).

Removal of copper from contaminated effluents is of great interest to meet discharge standards and prevent environmental degradation. It has conventionally been accomplished mainly by precipitation, ion exchange, and electrolytic technologies (Kadirvelu and Goel 2007); however, these technologies are limited by technical and economical constraints, especially when metal concentration in wastewater is low (Dupont et al. 2005). The passive removal of toxic heavy metals, such as cadmium, copper, zinc, lead, chromium, and mercury by many inexpensive biomaterials has been investigated, but brown algae have proven to be the most effective and promising substrates (Davis et al. 2000) Among the brown algae investigated for metal removal, *Sargassum* species have been identified as highly effective biosorbents, which are available in large amounts (Vieira and Volesky 2000; Davis et al. 2000; Herrero et al. 2011). In the Gulf of California, *Sargassum* species stand out among other macroalgae because of their large biomass. The estimated biomass of *Sargassum sinicola* Setchell & Gardner on the eastern coast of the Baja California Peninsula is >120,000 t (Casas-Valdez 2009). This species has demonstrated capacity for removing copper and cadmium from seawater in batch system (Patrón-Prado et al. 2010).

For practical operation of large-scale biosorption processes, continuous-flow, fixed-bed columns are often preferred since these systems are more efficient when a large volume of wastewater has to be treated (Chu 2004; Halim and Liew 2011). In this scenario, modeling of the parameters for continuous systems is needed to predict the quality of effluent under a wide range of operating conditions. The performance of such systems is usually described by a breakthrough curve,

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in which the concentration of contaminant in the effluent is plotted against time; however, the most appropriate method for assessing the biosorbent capacity is suggested to be the derivation of a series of sorption isotherms obtained from batch studies (Volesky et al. 2003). Furthermore, there are reports indicating greater removal capacity in continuous systems compared with that obtained in batch systems (Da Silva et al. 2002, Veit et al. 2009); however, there are also reports indicating the opposite (Vijayaraghavan and Prabu 2006; Sivaprakash et al. 2010).

The purpose of this study was to determine the biosorption capacity of copper (Cu^{2+}) by the brown macroalga *S. sinicola* in batch and continuous systems and the effect of flow rate, initial concentration of copper, and bed density on the biosorption capacity on the continuous system.

Materials and methods

Fresh samples of *Sargassum sinicola* were collected from the rocky seashore at Califin, Baja California Sur, Mexico (24°15′59.55″ N and 110°37′0.93″ W) in March 2009. The material was rinsed with fresh water to remove external salt, sand, and foreign biological material (Patrón-Prado et al. 2010). The samples were then dried to a constant weight, roughly chopped (particle size, 0.2–0.5 mm), and stored in polyethylene bags until used.

Cu^{2+} solutions were prepared with $CuCl_2$ salt at concentrations of 100, 200, 300, 400, 500, and 600 mg L^{-1}. A 50-mL volume of Cu^{2+} solution was placed in a propylene tube containing 0.5 g of macroalgae. The mixtures were stirred in an orbital shaker at 100 rpm for 24 h. The pH of the solution was adjusted to pH 5.5 during the first 2 h by adding 0.1 M NaOH or 0.1 M HCl. The algal biomass was then filtered through a 400-μm pore-size nylon mesh filter (Patrón-Prado et al. 2010). The filtrates were analyzed for Cu^{2+} concentrations by atomic absorption spectrometry. All experiments were performed in triplicate.

Metal uptake was determined by the formula $q = V\ S^{-1}(C_i - C_f)$, where q (in mg g^{-1}) is the amount of metal ions adsorbed on the biosorbent, V (in L) is the volume of metal-containing solution in contact with the biosorbent, C_i and C_f (in mg L^{-1}) are the initial and equilibrium (residual) concentrations of metal ions in the solution, and S (in g) is the amount of added biosorbent, on a dry weight basis.

The Langmuir adsorption model was used for estimating maximum metal adsorption by the biosorbent (Langmuir 1918). The Langmuir adsorption isotherm can be expressed as $q = (Q_{max}\ b\ C_f)\ (1 + b\ C_f)^{-1}$, where b is a constant related to the adsorption/desorption energy and represents the affinity between metal and seaweed, Q_{max} is the maximum biosorption with complete saturation of the surface (in mg g^{-1}), and C_f is the Cu^{2+} equilibrium concentration (in mg L^{-1}) in the solution.

The laboratory column (1.85 cm internal diameter) was packed with *S. sinicola* biomass to a height of 19 cm, which was held constant in all experiments while packed density was changed, modifying the amount of biomass in the column. The pH of the feed solution was adjusted to pH 5.5. Several breakthrough experiments were conducted using different feed flow rates (5, 10, 15, and 20 mL min^{-1}), initial Cu^{2+} concentration (50, 100, 150, and 200 mg L^{-1}), and bed density (100, 150, and 200 g L^{-1}). Solution samples were taken periodically at the column outlet and analyzed for copper concentration using atomic absorption spectrometry. All experiments were carried out in duplicate.

The characteristics and effectiveness of continuous biosorption were measured for breakthrough time (t_b) and exhaustion time (t_e) (Volesky 2001). These parameters were determined from the breakthrough curves, where t_b and t_e are defined as the time span during which the effluent concentration of Cu^{2+} was under 10 and 100 % of the initial concentration, respectively. The total amount of Cu^{2+} biosorbed in the column was calculated as the area above the breakthrough curve, using the equation:

$$q_c = \frac{F}{S}\int_{t=0}^{t=t_e} C_i - C_{Cu}\mathrm{d}t,$$

where t (in hours) is time, C_i and C_{Cu} are the initial and residual effluent concentrations (in mg L^{-1}), S is the algal biomass (in g), F is the rate flow (L h^{-1}) of the percolated solution, and q_c is the experimental biosorption capacity of the column (in mg g^{-1}).

The Thomas model was applied to experimental data to predict the breakthrough curves (Thomas 1944). This model can be expressed as follows:

$$\frac{C_{Cu}}{C_i} = \frac{1}{1 + \exp\left(\frac{K_{th} S\, Q_{C_{max}}}{F} - K_{th} C_i t\right)},$$

where $Q_{C_{max}}$ is the maximum biosorption capacity of the column (in mg g^{-1}), K_{th} is the rate constant (in L mg^{-1} h^{-1}), t is time (in hours), C_i and C_{Cu} are the initial and residual effluent concentration, F is the flow rate flow, and S is the algal biomass, defined previously.

Results

The isotherms of Cu^{2+} biosorption obtained from experimental and estimated data, using the Langmuir model in batch and continuous systems, are shown in Fig. 1. The maximum biosorption capacity (Q_{max}) of Cu^{2+} by *S. sinicola* in a batch system, according to the Langmuir

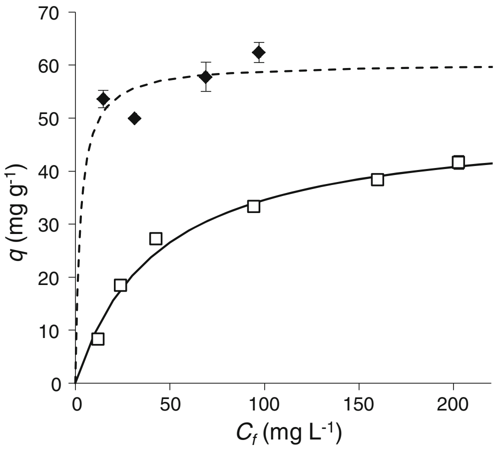

Fig. 1 Isotherm for Cu^{2+} biosorption onto *S. sinicola*. Experimental data from batch system (*empty squares*) and from continuous system (*filled diamonds*). *Lines* show results calculated using the Langmuir model

adsorption model, was 49.63±0.88 mg g^{-1} with a b constant of 0.023±0.001 L mg^{-1} (r^2=0.984). In the continuous system, removal capacity of *S. sinicola* (Table 1) reached its maximum when the flow rate of the Cu^{2+} solution is 10 mL min^{-1} (Fig. 2). The q_c values obtained at 5 (60.36± 4.15 mg g^{-1}) and 10 mL min^{-1} (62.39±1.91 mg g^{-1}) are not significantly different from each other (P=0.05).

The biosorption capacity of *S. sinicola* obtained from the batch systems was compared with that of the continuous system. The maximum biosorption capacity from the column system was calculated by fitting the experimental data obtained by changing the Cu^{2+} initial concentration into the Langmuir adsorption model provided a value for Q_{max} equal to 60.40±2.94 mg g^{-1}, with a b value of 0.38±0.22, which is 21 % higher than that obtained from the batch system (Fig. 1) .

The breakthrough curves obtained by changing the initial Cu^{2+} concentration are shown in Fig. 3. The lowest q_c value (49.98±0.28 mg g^{-1}) was observed at an initial Cu^{2+} concentration of 100 mg L^{-1}; the q_c value increases about 20 % when the initial Cu^{2+} concentration was increased to 200 mg L^{-1}. As the initial Cu^{2+} concentration increases, the breakpoint time decreases from 10.4 to 3.2 h, while steeper breakthrough curves and better Cu^{2+} removal occurred.

To predict the breakthrough curves, the Thomas model was used, showing a good fit with the experimental data, with a coefficient of determination above 0.90 (Table 1). The breakthrough curves obtained at different bed densities are shown in Fig. 4. The q_c values obtained had the highest removal capacity in the continuous system when the bed density was 150 g L^{-1}. Decreasing and increasing bed density resulted in lower Cu^{2+} removal, 13 and 11 % less, respectively. As the bed density increased, the breakpoint time increased from 1.28 to 3.5 h without a significant difference between the removal capacities observed at the lowest and highest densities.

Discussion

The ability of *S. sinicola* to remove Cu^{2+} in batch systems, is lower than that reported for other species of the same genus, such as *Sargassum muticum, Sargassum vulgare*, and *Sargassum filipendula,* ~71, ~59, and ~51 mg g^{-1}, respectively (Davis et al. 2000; Herrero et al. 2011). However, the Q_{max} value shown by *S. sinicola* is higher than quantities reported for most green and red macroalgae, such as *Codium vermilara* and *Chondrus crispus*, 16.9 and 40.5 mg g^{-1}, respectively (Romera et al. 2007).

In continuous systems, the maximum efficiency of *S. sinicola* to remove Cu^{2+} was 63 mg g^{-1}, which is similar to the efficiency reported for *Sargassum fluitans*, at 62 mg g^{-1} (Kratochvil et al. 1995), with both studies using

Table 1 Column data and Thomas model parameters obtained from breakthrough curves for Cu^{2+} biosorption on *Sargassum sinicola* at different flow rates, inlet copper concentrations, and bed densities

Column data			Experimental data			Thomas model parameters		
F (mL min^{-1})	C_i (mg L^{-1})	Bed density (g L^{-1})	t_b (h)	t_e (h)	q_c (mg g^{-1})	$Q_{C_{max}}$ (mg g^{-1})	K_{th} (L mg^{-1} h^{-1})	R^2
5	200	150	6.0	15.0	60.36±4.15	59.00±3.50	40.0±1.1E−04	0.997
10	200	150	3.2	10.0	62.39±1.91	63.00±2.10	80.0±2.9E−04	0.987
15	200	150	1.9	7.2	53.10±1.81	56.64±0.73	90.0±4.7E−04	0.991
20	200	150	1.1	5.0	49.99±3.12	52.50±0.91	110.0±8.2E−04	0.985
10	150	150	3.5	11.0	57.79±2.76	58.00±1.50	60.0±1.6E−04	0.996
10	100	150	5.8	13.2	49.98±0.28	50.15±0.20	100.0±2.3E−04	0.996
10	50	150	10.4	36.7	53.63±1.64	53.10±1.50	60.0±1.3E−04	0.991
10	200	100	1.28	9.75	54.23±2.00	53.30±1.80	60.0±5.4E−04	0.948
10	200	200	3.5	11.0	55.39±3.47	54.70±2.00	60.0±1.9E−04	0.994

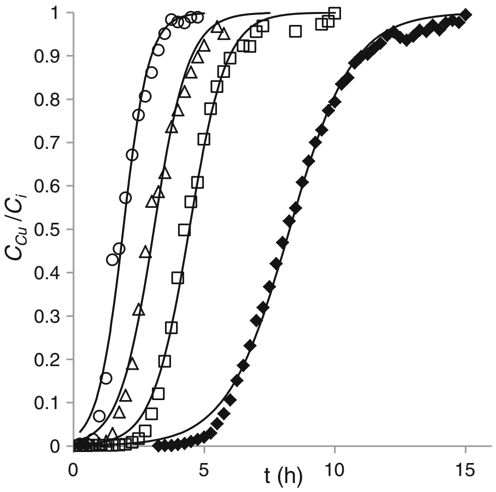

Fig. 2 Effect of flow rate on breakthrough curves for Cu^{2+} biosorption on *S. sinicola*: Initial metal ion concentration of 200 mg L^{-1}, and bed density of 150 g L^{-1}. Experimental data: 20 (*empty circles*), 15 (*empty triangles*), 10 (*empty squares*), and 5 mL min^{-1} (*filled diamonds*). *Lines* show results calculated using the Thomas model

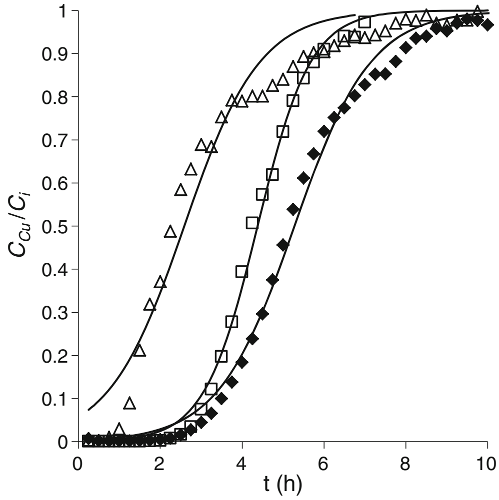

Fig. 4 Effect of biomass density on breakthrough curves for Cu^{2+} biosorption on *S. sinicola*: Initial metal ion concentration was 200 mg L^{-1}, and flow rate was 10 mL min^{-1}. Points are experimental data: 100 (*empty triangles*), 150 (*empty squares*), and 200 g L^{-1} (*filled diamonds*). *Lines* show results calculated using the Thomas model

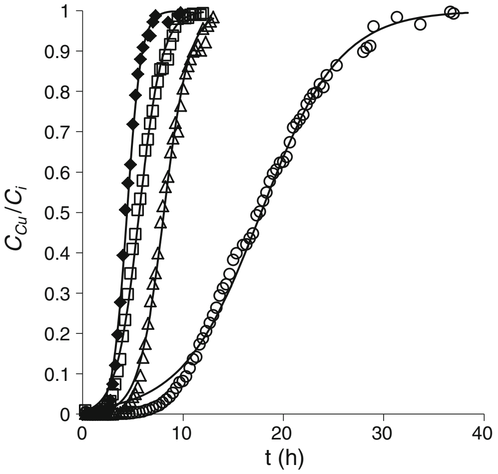

Fig. 3 Effect of initial metal ion concentration (C_i) on breakthrough curves for Cu^{2+} biosorption on *S. sinicola*: Flow rate was 10 mL min^{-1}, and bed density was 150 g L^{-1}. Points are experimental data: 50 (*filled circles*), 100 (*empty triangles*), 150 (*empty squares*), and 200 mg L^{-1} (*filled diamonds*). *Lines* show results calculated using the Thomas model

a flow rate of 10 mL min^{-1}. The efficiency of the genus *Sargassum* to remove Cu^{2+} is about two and four times higher than the efficiency of microorganisms, such as *Aspergillus niger*, *Saccharomyces cerevisiae*, and *Rhizopus delemar* that recorded ~14, ~27, and ~35 mg g^{-1} respectively (Tsekova and Petrov 2002; Godjevargova et al. 2004; Mukhopadhyay et al. 2008).

In continuous systems, as the flow rate increased from 5 to 20 mL min^{-1}, the breakpoint time decreased from 6.0 to 1.1 h. This may result from insufficient residence time of the Cu^{2+} in the column, that is, the Cu^{2+} left the column before equilibrium occurred (Aksu et al. 2002; Vijayaraghavan and Prabu 2006).

Comparing both systems, the higher removing capacity by continuous rather than batch systems was reported by Da Silva et al. (2002). They observed an increase of ~64.5 % in biosorption capacity of *Sargassum* sp. in a continuous system with respect to a batch system. Such differences have been attributed to the ions released by the biosorbent are maintained in solution in the batch system, which may cause interference in the biosorption process. In continuous systems, ions released by the biosorbent are continually removed from the system, which allows maintaining fixed conditions throughout the process (Da Silva et al. 2002).

The decline in breakpoint time from 10.4 to 3.2 h, when increasing the initial Cu^{2+} concentration, causes a steeper breakthrough curves and better Cu^{2+} removal, probably because the higher metal concentration raises the probability of interaction between metal ions and biosorbent. Higher initial metal concentration provides a greater driving force to overcome the mass transfer resistance of metals between aqueous and solid phases, which increases the probability of collision between metal ion and active sites and produces higher metal biosorption (Oztürk et al. 2004; Chen et al. 2005).

Low bed density increased the amount of empty spaces in the column, which decreases the probability of contact between Cu^{2+} and macroalgae. This leads to lower capacity to adsorb ions. Alternatively, the lower removal capacity, as density increases, may result from limited availability of metal or increased electrostatic interactions at the point of interference with active sites (Fourest and Roux 1992; Pradhan and Rai 2000).

In summary, the removal efficiency in batch and continuous systems using *S. sinicola* suggests that continuous system is a more suitable procedure for removing Cu^{2+} from aqueous solutions because of its higher biosorption capacity and quicker performance. Metal removal in the continuous system is affected by flow rate, initial concentration of the metal contaminant, and density. The Thomas model can be used to predict the breakthrough curves, but it underestimates the breakthrough time because it fails to accurately predict the Cu^{2+} concentration in the effluent during the first stage of the processes, when the C_{Cu}/C_i ratio is less than 0.15.

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