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Biosorption of copper by marine algae *Gelidium* and algal composite material in a packed bed column

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Abstract

Marine algae *Gelidium* and algal composite material were investigated for the continuous removal of Cu(II) from aqueous solution in a packed bed column. The biosorption behaviour was studied during one sorption–desorption cycle of Cu(II) in the flow through column fed with 50 and 25 mg l^{-1} of Cu(II) in aqueous solution, at pH 5.3, leading to a maximum uptake capacity of ≈13 and 3 mg g^{-1}, respectively, for algae *Gelidium* and composite material. The breakthrough time decreases as the inlet copper concentration increases, for the same flow rate. The pH of the effluent decreases over the breakthrough time of copper ions, which indicates that ion exchange is one of the mechanisms involved in the biosorption process. Temperature has little influence on the metal uptake capacity and the increase of the ionic strength reduces the sorption capacity, decreasing the breakthrough time. Desorption using 0.1 M HNO_3 solution was 100% effective. After two consecutive sorption–desorption cycles no changes in the uptake capacity of the composite material were observed. A mass transfer model including film and intraparticle resistances, and the equilibrium relationship, for adsorption and desorption, was successfully applied for the simulation of the biosorption column performance.

Keywords: Biosorption; Copper(II); *Gelidium*; Composite material; Column experiments

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1. Introduction

Industrialization and urbanization have led to an increase in metal contamination of aquatic environments. Biosorption may have a potential marketing advantage over other wastewater treatment technologies, because natural biomass is cheaper than the traditional activated carbon and ion exchange resins and it is environmentally friendly, particularly when waste biomass is used (Volesky, 2003). Although different kinds of biosorbents have been tested to remove several metals (Bailey et al., 1999; Babel and Kurniawan, 2003) only few have been commercialized. The algal biosorbent Alga SORB™ was developed by Bio-recovery Systems, Inc., using the freshwater alga *Chlorella vulgaris* to treat wastewater contaminated with metal ions (Volesky, 1990). B.V. Sorbex has developed different biosorbents for specific metal recovery using different types of biomass, including the algae *Sargassum natans*, *Ascophyllum nodosum*, *Halimeda opuntia*, *Palmyra pamada*, *Chondrus crispus* and *C. vulgaris* (Wase and Forster, 1997). Other commercial biosorbents have been produced, such as AMT-BIOCLAIM, using the *Bacillus* biomass (Volesky, 1990), Bio-Fix using a granular biosorbent consisting of a variety of biomasses including algae immobilized in porous polypropylene beads (Wase and Forster, 1997), MetaGeneR and RAHCO Bio-Beads (Atkinson et al., 1998; Gavrilescu, 2004). In all these systems, as it is the case for most sorption processes in general, the biosorbent is used as a packed bed contacting a downflow stream. This is the most effective configuration (Volesky, 2001). The performance of a column is related to the shape

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of the adsorption front, the length of the mass transfer zone (MTZ), and the profile of the effluent concentration, which depends on the nature of the adsorption isotherm and on the rate of mass transfer (Thomas, 1998). If there is enough time, the adsorbent close to the column inlet becomes saturated at the prevailing inlet fluid concentration, but a concentration gradient develops beyond the saturation zone (Thomas, 1998). The region of fading concentration is called the mass transfer zone (MTZ). The concentration profile is called the adsorption wave front and it is usually S-shaped (additional information in the Supplementary data file).

Biosorption of copper ions by algae *Gelidium* and a composite material (algal waste immobilized by polyacrylonitrile) has been tested in a batch system at different pH conditions, temperature and ionic strength (Vilar et al., 2007b). Desorption of copper ions using HNO_3 and Na_2EDTA as eluants has also been studied, showing a good elution efficiency at different solid to liquid ratios (Vilar et al., 2007a). In the present work, the performance of the same biosorbents was evaluated by using a packed bed column. To show the feasibility of possible applications of the biosorbents in two consecutive biosorption cycles, desorption experiments have been also conducted.

In order to provide the necessary information for process design and optimization, it was developed an effective mathematical model to describe the biosorption and desorption processes.

2. Methods

2.1. Preparation of biosorbents

An algal waste from agar extraction industry was immobilized with an organic polymer, (Polyacrylonitrile – PAN), and used in this study, as well as algae *Gelidium*, which is the raw material for agar extraction The characteristics and preparation of both biosorbents were described in previous works (Vilar et al., 2005a,b).

2.2. Preparation of copper solution

Copper(II) solutions were prepared by dissolving a weighed quantity of dehydrate copper(II) chloride in distilled water. Before the adsorption study, the pH of each test solution was adjusted to the required value with diluted HNO_3 and NaOH solutions.

2.3. Column experiments

Column experiments were conducted in a glass column (Sigma C 5794) with an inner diameter $ID = 2.5$ cm and length $L = 15$ cm, packed with algae *Gelidium* or composite material. An acrylic jacket surrounded the column body for temperature control. Adjustable plungers equipped with a 20 μm selective filters were attached to the top and bottom of the column. The apparent density of the biosorbents determined by mercury intrusion (PORESIZER 9320), is 1.34 and $0.25\ \mathrm{g\,cm^{-3}}$, respectively, for algae *Gelidium* and composite material (Vilar et al., 2007d).

A known quantity of algae *Gelidium* or composite material (≈ 10 g) was placed in the column. The copper solution (≈ 50 or $25\ \mathrm{mg\,l^{-1}}$) was pumped downflow through the column at a flow rate of $4\ \mathrm{ml\,min^{-1}}$ using a peristaltic pump (Gilson Minipuls 2). The flow rate was frequently measured during the experiment. Column effluent samples were collected regularly by a programmable fraction collector (Gilson FC 203B fraction collector) and analysed by atomic absorption spectrometry (GBC 932 Plus AAS). The effluent pH was recorded.

After column exhaustion, the loaded biomass was regenerated using 0.1 M HNO_3 at a flow rate of $8\ \mathrm{ml\,min^{-1}}$. The methodologies for collection and analysis of outlet samples were the same used for adsorption experiments. Finally, distilled water was passed through the bed until the pH of the effluent was around 5. The biomass was dried in the oven at 50 °C during two days and weighed. Before the next experiment the column was washed with nitric acid (20%) and distilled water. The experimental arrangement is shown in the Supplementary data file.

3. Results and discussion

The characterization of biosorbents surface by potentiometric titration and infrared spectrometry revealed the presence of two types of functional groups, carboxyl and hydroxyl groups (Vilar, 2006). The Sips distribution was used to obtain proton affinities to the different active sites (Vilar, 2006). Because carboxyl groups are acidic, at low pH they are protonated, and thereby become less available to binding metals, resulting in a decrease of copper uptake with pH.

Discrete and continuous equilibrium models (Vilar et al., 2007c) can be used to predict the equilibrium sorption experimental data at different pH values and copper concentrations. In this work, the equilibrium discrete model was used (see more in Supplementary data file), which becomes the simple Langmuir isotherm if pH influence is incorporated into the equilibrium constant (K_L). Model parameters, obtained for copper biosorption in a previous work (Vilar, 2006) are: $Q_{max} = 0.49 \pm 0.02$ and $0.177 \pm 0.009\ \mathrm{mmol\,g^{-1}}$ (maximum binding capacity), $pK_H = 4.3 \pm 0.1$ and 4.7 ± 0.1 (K_H – equilibrium proton constant ($\mathrm{l\,mmol^{-1}}$)); and $pK_M = 3.1 \pm 0.1$ and 3.5 ± 0.1 (K_M – equilibrium metal constant ($\mathrm{l\,mmol^{-1}}$)), respectively, for algae *Gelidium* and composite material.

The operating parameters for the different experiments are presented in the Supplementary data file.

3.1. Effect of inlet copper concentration

The increase of the inlet copper(II) concentration has a significant reduction effect on the breakthrough time as illustrated in Fig. 1a and b. This happens because satura-