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Copper desorption from *Gelidium* algal biomass

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ABSTRACT

Desorption of divalent copper from marine algae *Gelidium sesquipedale*, an algal waste (from agar extraction industry) and a composite material (the algal waste immobilized in polyacrylonitrile) was studied in a batch system. Copper ions were first adsorbed until saturation and then desorbed by HNO_3 and Na_2EDTA solutions.

Elution efficiency using HNO_3 increases as pH decreases. At pH = 1, for a solid to liquid ratio $S/L = 4\,g\,l^{-1}$, elution efficiency was 97%, 95% and 88%, the stoichiometric coefficient for the ionic exchange, 0.70 ± 0.02, 0.73 ± 0.05 and 0.76 ± 0.06 and the selectivity coefficient, 0.93 ± 0.07, 1.0 ± 0.3 and 1.1 ± 0.3, respectively, for algae *Gelidium*, algal waste and composite material.

Complexation of copper ions by EDTA occurs in a molar proportion of 1:1 and the elution efficiency increases with EDTA concentration. For concentrations of 1.4, 0.88 and $0.57\,mmol\,l^{-1}$, the elution efficiency for $S/L = 4\,g\,l^{-1}$, was 91%, 86% and 78%, respectively, for algae *Gelidium*, algal waste and composite material.

The S/L ratio, in the range $1–20\,g\,l^{-1}$, has little influence on copper recovery by using $0.1\,M\,HNO_3$.

Desorption kinetics was very fast for all biosorbents. Kinetic data using HNO_3 as eluant were well described by the mass transfer model, considering the average metal concentration in the solid phase and the equilibrium relationship given by the mass action law. The homogeneous diffusion coefficient varied between $1.0\times10^{-7}\,cm^2\,s^{-1}$ for algae *Gelidium* and $3.0\times10^{-7}\,cm^2\,s^{-1}$ for the composite material.

1. Introduction

The removal of toxic or valuable metal ions from wastewaters is of great importance from an environmental and industrial point of view. The biosorption of metal ions by algae (Yu et al., 1999; Hashim and Chu, 2004), industrial waste products (Ajmal et al., 1998; Babel and Kurniawan, 2003) and other natural materials (Chen et al., 1990; Cheung et al., 2003; Chu and Hashim, 2003) has revealed a promising property with potential for industrial use.

If the biosorption process is to be used as an alternative in wastewater treatment, the biosorbent regeneration may be crucially important to keep low processing costs and open the possibility to recover the extracted metal(s) from the liquid phase. The desorption process should yield metals in a concentrated form, which facilitates disposal and restores biosorbent for effective reuse (Wase and Forster, 1997; Volesky, 2003).

The desorption mechanism is similar to ion exchange, where metals are eluted from the biosorbent by an appropriated solution to give a small, concentrated volume of metal-containing solution. The biomass stripping can be achieved with a relatively inexpensive acid such as HCl, HNO_3 and H_2SO_4 (Tsezos, 1984; Kuyucak and Volesky, 1988;

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Aldor et al., 1995). Leaching of metal ions from contaminated soils using EDTA has been performed (Sun et al., 2001; Xueyi and Inoue, 2003), and the same eluant has also been used, as metal chelating agent, in the regeneration of macroalgae and microalgae (Zhou et al., 1998; Tan et al., 2002; Amorim et al., 2003).

Two important parameters to be considered in desorption process are the solid to liquid ratio (*S/L*) and the concentration factor (CR) defined as the ratio between metal concentration in the eluant and metal concentration at which the biomass was loaded (final concentration after the adsorption equilibrium). The *S/L* ratio should be as high as possible, since just a small volume of eluant is necessary to dislodge all the deposited metal. However, since metal biosorption is a reversible process, a high concentration of metal released into the solution may decrease desorption efficiency by leaving some residual metal still sorbed after a new equilibrium is obtained. Like *S/L*, a higher CR is better for the overall performance of the sorption process, leading to a higher capacity to concentrate the sorbate metal.

Combustion of the metal-laden biosorbent material to produce ash is an alternative to desorption and recycling. There may be cases where, if the biomass is cheap and highly available, recycle is no longer economical. The combustion of the biomass would produce ash with high metal concentration, which can be highly toxic. Alternatively, the biomass may be sterilised by microwave irradiation, if necessary, before encapsulation in an inert material for final disposal.

The biosorbents algae *Gelidium*, algal waste from the agar extraction industry and a composite material (waste+polymer), studied in this work, revealed a good performance in the uptake of copper ions. So, the reuse of the biomass was also studied. As HCl, HNO_3 and H_2SO_4 have similar elution efficiencies (Tsezos, 1984; Aldor et al., 1995), HNO_3 was selected because of its low price. EDTA also proved to be an effective eluant when compared with other complexing agents such as chloride, carbonate and bicarbonate (Aldor et al., 1995; Zhou et al., 1998).

2. Equilibrium model

In batch desorption tests, the desorbed sorbate (metal) stays in the solution and a new low-uptake equilibrium may be achieved. This leads to the concept of "desorption isotherm" whereby the equilibrium is strongly shifted towards the unbound sorbate species remaining in the solution. However, some residual sorbate may still be retained by the biosorbent to a varying degree.

Aldor et al., 1995, conclude that desorption of Cd is a reversible exchange process between the cadmium ions present in the biosorbent and the protons in the solution with a stoichiometric coefficient of 1.24, using HCl. This means that the exchange ratio is approximately one proton for one metal ion. So, establishing an exchange equilibrium between the proton and the metal ion bounded to the active sites in the biosorbent, and assuming that after the biosorbent saturation all the active sites are occupied by the metal ions and protons, the following equilibrium relation can be written:

$$\mathrm{LM_{(s)}} + \mathrm{H_{(aq)}} \rightleftharpoons \mathrm{LH_{(s)}} + \mathrm{M_{(aq)}}, \quad K_H^M \tag{1}$$

where L represents the active site negatively charged, M the metal ion and H the proton. The ion exchange equilibrium can be described by the selectivity coefficient, K_H^M, obtained by the mass action law applied to ion exchange on resins (Helfferich, 1995):

$$K_H^M = \frac{q_M C_H}{q_H C_M}, \tag{2}$$

where q_M is the equilibrium metal concentration in the solid phase (mmol metal ion g^{-1} biosorbent), q_H the equilibrium proton concentration in the solid phase (mmol proton ion g^{-1} biosorbent), C_M the metal concentration in the liquid phase (mmol metal ion l^{-1} solution) and C_H the proton concentration in the liquid phase (mmol proton ion l^{-1} solution).

Considering the total mass balance in the liquid and solid phases,

$$C_T = C_{M_0} + C_{H_0} = C_M + C_H = \text{constant}, \tag{3}$$

$$Q_{max} = q_M + q_H = \text{constant}, \tag{4}$$

where C_T is the total (metal+protons) concentration in solution (mmol l^{-1} solution), C_{M_0} the initial concentration of the metal ion in solution after the adsorption phase (mmol l^{-1} solution), C_{H_0} the initial concentration of protons in solution after the adsorption phase (mmol l^{-1} solution) and Q_{max} the total concentration of the binding active sites (mmol g^{-1} biosorbent).

On replacing Eqs. (3) and (4) in Eq. (2) and rearranging, we can obtain the following equation for the mass action law:

$$q_M = \frac{K_H^M Q_{max} C_M}{C_T + (K_H^M - 1) C_M}. \tag{5}$$

The mass action law parameters were obtained by determining the equilibrium concentration in the liquid and solid phases, at different pH values, using the same initial biosorbent metal loading. The value of Q_{max} was obtained by potentiometric titrations of carboxylic groups (0.36 ± 0.01, 0.23 ± 0.05 and 0.16 ± 0.01 mmol g^{-1}, respectively, for algae *Gelidium*, algal waste and composite material) (Vilar, 2006).

Comparing the Langmuir equation (Langmuir, 1918), which assumes free sites, with the mass action law, $K_H^M = K_L/C_H$ if the equilibrium Langmuir constant is defined as $K_L = (Q_{max} - q_M)C_M/q_M$. The difference between the two models may be especially marked at low metal ion concentration, considering a constant pH (Crist et al., 1994).

3. Mass transfer desorption model

Desorption of metals may be carried out under acidic conditions. During the desorption process, metals ions loaded to biomass are replaced by protons diffusing in from the bulk eluant solution. Then, the eluted metal ions can diffuse through the permeable biomass towards the particle surface. Finally, the ions diffuse across the stationary liquid layer (film) that surrounds the biomass particles into the bulk solution. The main resistance to the overall desorption process is the internal diffusion (Yang and Volesky, 1996). In