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Biosorption of cadmium with brown macroalgae

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HIGHLIGHTS

- *Lessonia nigrescens* and *Durvillaea antarctica* adsorb cadmium efficiently.
- The sorption kinetics for *Durvillaea antarctica* followed a pseudo second order model.
- The *Lessonia nigrescens* sorption could better be described by first order kinetics.
- Langmuir isotherm model was adequate for both seaweeds studied.

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ABSTRACT

Sorption experiments for cadmium removal using two brown macroalgae *Lessonia nigrescens* and *Durvillaea antarctica* were carried out. Although both types of algae were capable of retaining cadmium, differences in their performance were observed. The optimum pH was 3.7 ± 0.2, and to achieve the equilibrium, 5 days of contact time were necessary for both biosorbents. The maximum experimental uptake obtained was similar for the two biosorbents: 95.3 mg Cd g^{-1} by *D. antarctica* and 109.5 mg Cd g^{-1} by *L. nigrescens*.

The Langmuir model described the equilibrium sorption isotherms very well for both biosorbents and the Lagergren pseudo primer order model described the sorption kinetics for *L. nigrescens* satisfactorily and the Ho and Mckay pseudo second order model for *D. antarctica*. It was found that cadmium uptake by *D. antarctica* was faster than by *L. nigrescens*.

1. Introduction

Industrial activities, such as mineral processing and extractive metallurgical operations produce large quantities of wastewater containing high levels of heavy levels of heavy metals (Hansen et al., 2006; Antunes et al., 2003; Hansen et al., 2010; Davis et al., 2000; Deng et al., 2007; Ahalya et al., 2003; Nilanjana et al., 2008). This is a major environmental problem in Chile, since this country is one of the world's largest copper producers (Jamasmie, 2012). Heavy metals are highly toxic elements that can accumulate throughout the food chain (Uslu et al., 2003; Bishnoi et al., 2004; Wahab, 2007). Mercury, cadmium, lead and arsenic are some examples of potentially hazardous elements (Lodeiro et al., 2006, 2005; Mata et al., 2008). Poon reported cadmium concentrations in various waste waters ranging from 0 to 1000 mg L^{-1}, for example for plating rinse waters: 48–240 mg L^{-1} and lead mine acid drainage: up to 1000 mg L^{-1} (Poon, 1984) Cadmium has a half life of 10–30 years in the human body (Naja et al., 2010) and the toxicity of this element produces renal disfunction, bone degeneration, liver damage and others health effects (Sari and Tuzen, 2008; Lee Kang et al., 2012; Bernard, 2008). Heavy metals present in wastewaters are normally removed by different treatments, such as chemical precipitation, reverse osmosis, electrodialysis, and ion exchange. These technologies present the disadvantages of being expensive, using great amount of reagents, generating large amount of toxic sludge, or being inefficient when treating large volumes with low heavy metal concentration (Kaewsarn and Yu, 2001; Herrero et al., 2008). In recent years, biosorption has attracted the attention as an alternative technology to treat large volumes of diluted metal-contaminated wastewater. Biosorption uses non-living biomass to remove the heavy metals from the solution. Seaweeds have shown good results as biosorbents of heavy metals (Murphy et al., 2007; Hashim and Chu, 2004; Srinivasa Rao et al., 2005). Biosorption by seaweeds is based on several mechanisms, including ion-exchange and complexation with oxidation/reduction reactions in some cases (Davis et al., 2003). All along the Chilean coast, two types of brown seaweeds are found named *L. nigrescens* and *D. antarctica*, and these will be used as biosorbents to remove cadmium from

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wastewater in the present work. Brown seaweeds have alginic acid and fucoidan in their structure; main responsibles for the heavy metal removal from solutions (Naja et al., 2010).

The objectives of this work are: (i) to evaluate two types of brown seaweeds – *L. nigrescens* and *D. antarctica* – to be used as bisorbents of cadmium, (ii) to determine the wastewater pH (in the range between pH 3.2 and 5.7) where the metal retention is optimal, (iii) to determine the maximum adsorption capacity of these seaweeds, (iv) to determine the adsorption isotherms, using mathematical models to adjust the results, and (v) to determine the biosorption kinetics, using mathematical models.

2. Background

The biosorption process involves a solid phase and a liquid phase containing the dissolved species to be sorbed. From the biosorption experiments it is possible to evaluate quantitatively the retention capacity of a metallic contaminant by the biosorbent. The experimental conditions such as initial metal concentration, biosorbent mass-to-solution volume ratio (M/V) and solution pH have influence on the metal retention and equilibrium achieved. The retention is also a function of the size and shape of the biosorbent used, and therefore the actual shape of the biosorbent must be specified.

The equilibrium isotherms are plots that relate the retention of the metal by the biosorbent and the equilibrium concentration of the metal remaining in the solution. The name "isotherm" is due to the initial conception of the sorption experiments, which must be done at constant temperature. However, the effect of temperature in biosorption is not as important as other influencing factors, such as solution pH (Volesky, 2004).

The retention of the solute by a biosorbent can be estimated by a mass balance:

$$C_i \cdot V = C_{eq} \cdot V + q \cdot M \tag{1}$$

where C_i and C_{eq} are the initial and equilibrium concentration of the metal, respectively, V is the volume of the liquid phase, q is the metal retention by the biosorbent and M is the mass of dry biosorbent.

$$q = \frac{V \cdot (C_i - C_{eq})}{M} \tag{2}$$

There are two models typically used to adjust the adsorption isotherms. These are the Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1907) models, both of them are used for modeling of the biosorption equilibrium for single component systems at constant temperature and pH.

There are two commonly used kinetic models to adjust the kinetic experimental data: the Lagergren pseudo-first order model (Lagergren, 1898) and the Ho and McKay pseudo-second order model (Ho and Mckay, 1999).

2.1. Langmuir isotherm

This model is based on the assumption that active surface sites exist on the solid material, to which the metals are adsorbed. The ions are fixed on a monolayer on the surface; there is no penetration of ions into the interior of the adsorbent. The model can be expressed in the following manner:

$$q_{eq} = \frac{q_m \cdot b \cdot C_{eq}}{1 + b \cdot C_{eq}} \tag{3}$$

where q_{eq} is the equilibrium concentration of the metal on the biomass, q_m is the maximum concentration of the metal on the biomass, b is a coefficient related to the affinity between the biosorbent and the metal and C_{eq} is the equilibrium concentration of metal in the solution. High values of b indicate a high affinity for the biosorbent and show a steep initial slope in the isotherm plot.

2.2. Freundlich isotherm

This model is characterized by being an empirical equation, which is not limited to a finite adsorption capacity as the Langmuir model. Therefore, it is applicable for low and medium concentrations of solutes:

$$q_{eq} = K \cdot C_{eq}^{\frac{1}{n}} \tag{4}$$

where K is a constant related to the adsorption capacity and $1/n$ is related to adsorption intensity.

2.3. Pseudo-first order kinetics: Lagergren model

One of the most applied models to describe the biosorption kinetics is the Lagergren model. This model is based on the assumption that for each metallic ion, one adsorption site of the biosorbent is assigned. The pseudo-first order rate expression of Lagergren is given by the following expression:

$$\frac{dq_t}{dt} = k_{ad} \cdot (q_{eq} - q_t) \tag{5}$$

When Eq. (5) is integrated:

$$q_t = q_{eq}(1 - e^{-k_{ad}t}) \tag{6}$$

where q_t is the metal adsorbed by the biosorbent at time t, q_{eq} is the adsorbed metal in equilibrium conditions and k_{ad} is a first order adsorption constant.

2.4. Pseudo-second order kinetics: Ho and Mckay model

Another widely used model, the Ho and Mckay model, supposes the adsorption of divalent metal ions onto the adsorbent using two active sites. The pseudo-second order kinetic model is expressed as:

$$\frac{dq_t}{dt} = k \cdot (q_{eq} - q_t)^2 \tag{7}$$

where k is a second order adsorption constant.

Separating the variables in Eq. (7), then integrating for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, gives:

$$\frac{t}{(q_{eq} - q_t)} = kt + \frac{1}{q_{eq}} \tag{8}$$

When rearranging Eq. (8), the following is obtained:

$$\frac{t}{q_t} = \frac{1}{k} + \frac{t}{q_{eq}} \tag{9}$$

3. Experimental

3.1. Reagents

The cadmium solutions were prepared by dissolving $Cd(NO_3)_2{\cdot}4H_2O$ (analytical grade) in distilled water. In order to adjust pH either HCl or NaOH (both analytical grade) was used.

3.2. Analytical

Each liquid sample was filtered through a N° 131 grade filter paper by a vacuum pump. The cadmium concentration in the