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Biosorption of lead from acidic aqueous solutions using *Durvillaea antarctica* as adsorbent

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ABSTRACT

Biosorption of Pb^{2+} from aqueous solutions by dried, brown algae *Durvillaea antarctica* was studied. A series of batch sorption experiments were carried out, where lead concentration was measured with time in a solution in contact with the algae. The Pb^{2+} uptake efficiency was determined for different (a) pH levels in the solution (1.5–4), (b) initial lead concentration (200–1200 mg L^{-1}), and (c) contact time between solution and algae (10–10,080 min).

The biosorption kinetics and isotherms were determined from the experimental batch sorption data. The results showed that the second order kinetic model of Ho and Mckay described the biosorption process well; the rate constants ranged from 0.137 to 0.349 mg g^{-1} min^{-1} as a function of initial metal concentration. Changes in the pH of the solution did not affect the kinetics significantly for the pH range studied (1.5– 4). Considering conventional empirical isotherm models, the Langmuir model predicts slightly better the biosorption equilibrium at ambient temperature than the Freundlich model at the pH level studied. The Langmuir model showed maximum uptake value of 135.1 mg g^{-1} and the affinity constant was 2.55 L mg^{-1}.

The aim for future work should be focussed on how to transfer the positive lead batch sorption results to a continuous process that treats lead containing wastewater.

1. Introduction

Mining has crucial importance for the Chilean economy, since Chile is one of the world's largest copper producers – with more than 30% of the worldwide copper production (COCHILCO, 2009). A minor but still important production of lead adds to the overall mineral processing scenario of Chile. During the concentration and processing of different minerals considerable volumes of residues – either liquid or solid – are generated. The liquid residues – or wastewaters – produced by mining activities contain lead, copper, arsenic and other inorganic species in concentrations that exceed the local legal threshold values (Chilean Republic, 2000). Existing treatment methods such as sulphide or hydroxide precipitation create sludge that is difficult to handle. Furthermore, these methods consume considerable amounts of reagents in order to precipitate, coagulate and flocculate the contaminants.

Lately, focus has been turned into more environmentally friendly methods. One of these is biosorption, where heavy metals are removed from the wastewater by materials of biological origin (Volesky and Holan, 1995; Fiset et al., 2008). Biosorption is a physical–chemical process that includes the phenomena of adsorption, absorption and exchange of molecules and ions by different materials such as algae, fungi, or fruit, vegetable and other organic residues (Volesky and Holan, 1995; Ho et al., 2000; Hansen et al., 2010). These materials can be used either directly or by simple transformation (Das et al., 2008), and in some cases these can be regenerated and reused several times (Bakir et al., 2010). Biosorption is more feasible for low concentration wastewaters and does not generate toxic residues, and metals can be recovered easily by desorption or destruction of the biosorbent. For lead removal in particular, several materials have been suggested but mostly for removal of lead in around pH neutral solutions, whereas mining wastewaters typically are acidic. Table 1 shows lead sorption capacities of selected sorbents found in literature.

Durvillaea antarctica is a very abundant brown algae all along the coast of Chile. It is not a process residue as other sorbents mentioned in Table 1, and therefore independent of different process conditions. Furthermore, the high content of alginates makes its potential for heavy metal uptake obvious (Kelly and Brown, 2000). When harvested, it is physically and chemically stable over relatively long time periods, which makes it suitable as a sorbent. In contrast to other sorbents listed it could be used as dead biomass, and the sorbent behaviour could be compared to ion

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Table 1
Lead sorption capacities for selected sorbents listed in the literature.

Material	Sorption capacity [mmol g^{-1}]	pH	Reference
Waste beer yeast	0.028	>4	Han et al. (2006)
Cereal chaff	0.06	5.5	Han et al. (2005)
Natural zeolite	0.08	5	Matheickal and Yu (1996)
Olive tree pruning waste	0.12–0.16	5	Blázquez et al. (2011)
Granular activated carbon	0.15	–	Muraleedharan et al. (1995)
Bacterial cells	0.37	–	Vecchio et al. (1998)
Sphaerotilus natans (Bacterium)	0.39	4	Pagnanelli et al. (2003)
Penicillum oligosporus (Fungus)	0.59	5	Ariff et al. (1999)
Padium pavonia (Seaweed)	1.05	4.5	Jalali et al. (2002)
Sargassum natans (Brown algae)	1.22	3.5	Holan and Volesky (1994)
Modified orange peel	1.22	4.5–6	Xuan et al. (2006)

exchange resins. Especially it would be interesting in evaluating the lead sorption capacity of *D. antarctica* in low pH solutions, where only few biosorbents are efficient.

This work focuses on the biosorption method for lead removal from acidic aqueous solutions using the algae *D. antarctica* as biosorbent. The objectives of the present work are: (i) to determine the lead removal capacity of *D. antarctica* – especially at low pH, (ii) to realize kinetic biosorption tests to determine initial biosorption velocities (with the use of common kinetic models) and final equilibrium concentrations, (iii) to evaluate the effect of pH on the biosorption process, and (iv) to determine and fit adsorption isotherms to conventional mathematic models.

2. Experimental

2.1. Reagents

Lead solutions were prepared by dissolving analytical grade lead nitrate [$Pb(NO_3)_2$] 99% (Loba Chemie), in distilled water. pH was adjusted by addition of hydrochloric acid fuming 37% GR for analysis (Merck) or by addition of sodium hydroxide NaOH (5 M) prepared by dissolving sodium hydroxide pellets extra pure 98% (Loba Chemie).

2.2. Analytical

Each liquid sample was filtered through N° 131 grade filter paper (Advantec) by a vacuum pump (Welch, model 2522). The lead concentration in the filtrate was determined by Atomic Absorption Spectrophotometry in flame (Varian, model SpectrAA 55) according to Chilean standard NCh 2313/10 Of. 96. In order to have a mass balance control, after a couple of experiments the algae was dried, and lead was determined according to the ISO 11466 (1995) procedure for determination of trace metals in solid materials. In general, the mass balance showed less than 5% error. pH was measured with a combined pH electrode connected to a Orion PerpHecT logR model 370 pH meter.

2.3. Biosorbent preparation

The *D. antarctica* samples were collected in the bay of Valparaiso, Chile. Only the leaves were used. After sampling, the algae was washed several times in tap water and then in distilled water in order to remove any salt present. Thereafter the algae were dried in an oven (TS Tau Steril Automatic, Type Clinic) at 50 °C for 48 h. The dry alga was cut into small pieces of around 0.5–1 cm size pieces. The natural background content of lead in the algae was found to be 1.2 ± 0.4 mg/kg dry matter using the ISO 11466 (1995) procedure for determination of trace metals in solid materials.

2.4. Experimental plan

The conditions for the different biosorption experiments are shown in Table 2. 4 [g] of algae was placed in 500 [mL] solution in all experiments – giving a biomass/solution volume ratio of 8 [g L^{-1}]. All experiments were done without agitation. The temperature during experiments was monitored but not controlled (always in the range: 20–25 [°C]). pH was kept constant by adding drops of either HCl or NaOH solutions. The total volume did not increase more than 2% in the experiments.

3. Results and discussion

In this work, the lead retention by the algae is calculated from a simple mass balance, where the metal retention by the algae is assumed to correspond to the difference between the initial and final lead concentration in the solution. This can be summarized in the following manner:

$$C_i\left[\frac{\text{mg}}{\text{L}}\right]\cdot V[\text{L}] = C_f\left[\frac{\text{mg}}{\text{L}}\right]\cdot V[\text{L}] + q\left[\frac{\text{mg}}{\text{g}}\right]\cdot M[\text{g}]$$

$$Q = \frac{V\cdot(C_i - C_{eq})}{M}$$

where q is the metal retention by the biosorbent [mg metal g^{-1} biosorbent], C_i is the initial metal concentration in the solution [mg L^{-1}], V is the solution volume [L], C_f is the final concentration of the metal in the solution [mg L^{-1}], and M is the biosorbent mass [g]. In the case, where adsorption equilibrium is reached, C_f equals the equilibrium concentration in the solution.

Table 2
Experimental conditions.

Type of experiment	Initial lead concentration [mg/L]	M/V [g L^{-1}]	pH	Time [min]
Biosorption kinetics	400, 800, 1200	8	1.5 ± 0.1 2.5 ± 0.1 4.0 ± 0.2	10, 20, 30, 45, 60, 120, 180, 300, 1440, 4320, 10,080
Adsorption Isotherms	200, 400, 500, 600, 800, 1000, 1200	8	1.5 ± 0.1	10,080

M/V: dry biosorbent mass [g]/lead solution volume [L] ratio.