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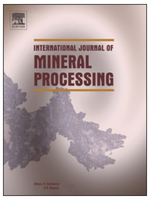

Binary biosorption of copper and lead onto pine cone shell in batch reactors and in fixed bed columns

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ABSTRACT

In the present work, biosorption of copper(II) in the presence of lead(II) ions by native pine cone shell (PCS) was investigated in batch and packed bed reactors. Particularly, it provides new information regarding binary biosorption of metals in continuous flow. The behavior of competitive Cu(II) and Pb(II) biosorption in batch was successfully described by the multicomponent Sips model, obtaining maximum capacities for Cu(II) and Pb(II) of 6.52 mg/g and 17.41 mg/g, respectively. The single-metal biosorption uptake capacities of the biomass for copper and lead were slightly inhibited by the presence of lead and copper, respectively. Pine cone shell removed the target metal ions in the affinity order of Pb(II) > Cu(II) quantified in mass basis. Factors such as covalent index of the metal ions may contribute to this result. In tests carried out in a packed-bed column, the biosorption capacity for Pb(II) (17.85 mg/g) was also higher than copper one (9.38 mg/g), confirming the higher selectivity of the pine cone shell for lead over copper ions in continuous system too. Finally, desorption studies indicated that Cu,Pb-loaded PCS could be easily eluted by 0.3 M HCl.

1. Introduction

Contamination of natural habitats by heavy metals through industrial and agricultural activities has the potential of affecting the health of living beings and the environment due to the toxicity of these substances and the difficulty in their remediation (Bahadir et al., 2007; Pérez-Marín et al., 2008).

In recent years, different agricultural by-products such as *Zea mays*, tea leafs, walnut shells, pine sawdust, agave bagasse, olive tree pruning wastes, and olive stones have been very often used as biosorbents of heavy metals (Calero et al., 2013; García-Rosales et al., 2012; Hodaifa et al., 2013; Martín-Lara et al., 2012; Ronda et al., 2013; Saqib et al., 2013; Velazquez-Jimenez et al., 2013; Xi and Chen, 2014; Zou et al., 2013). Biosorbents can attract and bind heavy metals by complex processes that comprise of ion exchange, surface precipitation, surface adsorption, metal detoxification and transformation. A great variety of studies have focused on copper and lead biosorption in single metal or binary mixtures by means of batch systems (Christoforidis et al., 2015; Kan et al., 2015; Moyo et al., 2015; Ronda et al., 2014).

Ronda et al. (2014) studied the copper biosorption in the presence of lead onto olive stone and pine bark in batch, and they observed that the lead did not produce an important interference onto copper biosorption when both metal ions are present in solution for tested conditions.

Christoforidis et al. (2015) studied the removal of Cu(II) by *Cystoseira crinitophylla* biomass in batch system and they demonstrated that this biosorbent can be used effectively for decontaminating aqueous solutions contaminated with copper. Same results were obtained by Kan et al. (2015) in the removal of copper (II) by mushroom biomass. Moyo et al. (2015) prepared a low cost biosorbent from marula seed husk (*Sclerocarya birrea*) biomass for removal of Pb(II) and Cu(II) from aqueous solution in batch systems and they showed that the biosorbent had better performance for Pb(II) than Cu(II) removal.

However, biosorption can be operated not only in batch reactors but also in fixed-bed reactors. The column system offers optimum conditions for enhancing the driving force (due to concentration gradient), which improves biosorption efficiency and mass transfer performance. A number of fixed-bed column investigations have been conducted in single systems (Chao et al., 2014; Christoforidis et al., 2015; Cruz-Olivares et al., 2013; Sarma et al., 2015) but, today, very few studies have focused on the analysis of breakthrough curves on binary biosorption on packed bed reactors.

Pine trees are evergreen, coniferous, and fast-growing resinous trees which are widely grown in most temperate regions in relatively dense stands. Pines are among the most commercially important trees which are widely used in lots of industries. They generate acidic decaying needles that constitute a surface layer with open structure while conserving the soil moisture. Moreover, the needles are used as an agricultural commodity for mulching; however, the leaves together with barks comprise the major fraction of pine wood wastes when the tree is harvested (Pote et al., 2004). Similar to other wood wastes, bark, branches, leaves, and other parts of pine trees, are produced in the forest

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industries (Claassen et al., 1999; Tjoelker et al., 2007; Wingren et al., 2003). Despite their potential for biofuel production or as biosorbent of pollutants, these residues are currently destined for landfills or burned to produce heat (Blázquez et al., 2011a, 2012; Değirmen et al., 2012; Gundogdu et al., 2009; Luo et al., 2010; MacFarlane, 2009; Ofomaja and Naidoo, 2011; Tatàno et al., 2009).

The main aim of this study was to study pine cones as biosorbent of copper from aqueous solutions in batch and packed bed reactors analyzing the effects of the presence of lead on copper removal and the possibility of regeneration and reuse.

2. Materials and methods

2.1. Biosorbent material

Pine cone shell (PCS) was provided by Carsan Biocombustibles S.L. factory from Granada (Spain). The biomass was ground with an analytical mill (IKA MF-10) and sieved into fractions below 1 mm. All fractions collected below mesh size of 1 mm were chosen for the characterization and biosorption tests without any pre-treatment.

2.2. Characterization of PCS

Elemental analysis was performed with an EA 1108 CHNS elemental analyzer (Fison's Instruments). The oxygen content was obtained indirectly by difference.

Surface area and pore size distribution were determined by mercury intrusion porosimetry (MIP) generated using a mercury porosimeter (Quantachrome, model Poremaster 60).

The particle size range of the biosorbent was determined by milling 100 g of PCS (from an initial size ranging between 4 mm and 8 mm), passing them through different sieves and shaken for 10 min with a bottom pan placed to collect samples finer than the meshes.

Amount of acidic/basic functional groups was determined by potentiometric titration using an automated titrator (Metrohm 794 Basic Titrino). Biosorbent suspensions of PCS (2 g of solid in 50 mL of deionized water) were fluxed by N_2 to remove CO_2 and titrated by standard solutions of 0.1 M NaOH (basic branch) and 0.1 M HCl (acid branch). After each addition of titrant (NaOH or HCl) the suspension was allowed to reach equilibrium under magnetic stirring and then the pH was measured by a pH meter.

2.3. Preparation of Cu(II) and Pb(II) solutions

Stock solutions of Cu^{2+} and Pb^{2+} were prepared by dissolving the necessary amount of $Cu(NO_3)_2 \cdot H_2O$ and $Pb(NO_3)_2 \cdot 3H_2O$ in distilled water. They were further diluted to obtain desired concentrations of the metals. The pH of the solution was adjusted using 0.1 M HCl and 0.1 M NaOH solutions.

2.4. Batch biosorption experiments

Biosorption experiments were made by suspending an amount of 1 g of biosorbent with 100 mL of the synthetic two-metal solutions in a 150 mL jacketed reactor connected to a thermostat-controlled bath in order to keep temperature at 25 °C. The pH was kept constant at a value of 5, since it is the optimal value of pH for copper and lead biosorption in monometallic systems and since the precipitation of these metals do not occur at this value. Subsequently, when metal ions and biosorbent have been in contact during 120 min, the liquid phase is taken out from the reactor and centrifuged for 10 min. Finally, the supernatant solution is filtered and analyzed for determining metal concentrations by a flame atomic absorption (AA) spectrophotometer (Perkin Elmer, Model AAnalyst 200). All experiments were performed in duplicate.

Metal removal efficiencies were calculated using the following equation:

$$\text{Removal } (\%) = \frac{(C_0 - C_e)}{C_0} \cdot 100 \tag{1}$$

and the amount of metal uptake as follows:

$$q_e = \frac{(C_0 - C_e)}{m} \cdot V \tag{2}$$

where q_e (mg/g) is the amount biosorbed at equilibrium, C_0 (mg/L) and C_e (mg/L) are the initial and the equilibrium metal concentrations, respectively, m (g) is the mass of biosorbent and V (L) is the volume of solution.

2.5. Continuous biosorption experiments

For continuous biosorption experiments, a jacket glass column with an internal diameter of 15 mm and a length of 230 mm was packed with a known mass of biosorbent. To enable a uniform inlet flow of the solution into the column, glass beads of 5 mm diameter were placed to attain a desired height. The glass bead layer at the bottom of the column helped in even distribution of the metal solution through the top of the column and also prevented the removing of the sorbent at the bottom. The metal solution at desired initial concentration was pumped in up-flow mode at a constant flow rate using a peristaltic pump. Previously, the best biosorption conditions were obtained by performing a previous factorial design varying inlet metal concentration, bed depth and flow rate. Binary biosorption tests were performed under these conditions. Column effluent samples were collected at frequent time intervals and analyzed for effluent metal concentration. The Cu(II) and Pb(II) in the remaining solution were analyzed in an Atomic Absorption Spectrometer (Perkin-Elmer, model AAnalyst 200). All experiments were performed in duplicate.

2.6. Continuous desorption experiments

Desorption studies to regenerate the native PCS biosorbent were conducted using 0.3 M HCl. Reusability of biosorbent was studied by four cycles of alternating biosorption/desorption experiments with the supplement of a solution of 100 mg/L of Cu(II) and 100 mg/L of Pb(II) at the beginning of each cycle. The elution curves obtained for the displacement of the metals of PCS were performed in dynamic system, using the same flow rate values held for the biosorption, and evaluated with respect to the amount of eluted metal.

3. Results and discussion

In most of the literature on biosorption, units of mg/L for concentrations and mg/g for biosorption capacities are commonly used. Similarly, in most of the regulations on discharge of heavy metals in aqueous media data are presented in mg/L or μg/L. Therefore, this paper has been designed in mass basis from the point of view of its experimental realization and all units are expressed in mass basis. However, many of the results, particularly biosorption capacities, were also expressed on a molar basis, to enhance the discussion of results.

3.1. Characterization of PCS

Results of physical–chemical characterization of PCS are presented in Table 1. Elemental analysis results showed that PCS has an elemental composition consisting mainly of carbon and oxygen. The moisture content was of 9.07%. This low moisture content facilitates the preparation of this solid as biosorbent, since they require no drying before to use.

The results show that the PCS pores are mesopores with an average pore width of 45.5 Å and total pore volumes of 1.344 cm^3/g.