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Effect of lead in biosorption of copper by almond shell

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ABSTRACT

In this study, the effect of Pb(II) in biosorption of Cu(II) by almond shell from a binary metal mixture was studied and compared with the single metal ion situation in a batch stirred system and in a continuous system. It was observed that copper biosorption yields and copper equilibrium uptakes were slightly reduced by the presence of lead. This antagonistic action can be related with competition phenomena between metal cations in solution for active sites presented on almond shell. The affinity of Pb(II) for almond shell was higher than that of Cu(II). In binary systems in a batch stirred system, extended Langmuir model and extended Sips model were used to fitting experimental data. Biosorption equilibrium data fitted very well to both models in the concentration range studied. But, although differences between the fitting of these two models were insignificant, it was obtained that extended Sips model reproduced better the experimental results than the Langmuir one. The maximum biosorption capacities obtained for Cu(II) and Pb(II) were approximately 9.0 mg/g and 13.7 mg/g, respectively, Finally, breakthrough curves for continuous removal of Cu(II) from single and binary metal solutions were reported. Column competitive biosorption data were evaluated in terms of the biosorption (equilibrium) capacity of the column, the amount of metal loading on almond shell surface, the total biosorption yield, breakthrough and exhausted time.

1. Introduction

Heavy metals are used in different industries such as metal plating, mining operations, battery manufacturing, tannery and fabrication [1]. The presence of toxic heavy metals over the permissible levels in the environment is a severe public health problem. Thus, governments have established environmental restrictions with regard to the quality of wastewater, forcing industries to remove metals from their effluents before discharging. Lead is one of the toxic heavy metals which are common pollutants of the environment. In humans, all measured effects of lead on living organisms are adverse, including those related to survival, growth, learning, reproduction, development, behavior, and metabolism. Lead has no known essential biological function, and all lead compounds are potentially harmful or toxic. Besides lead, copper is also a common and serious environmental pollutant. Although it is an essential dietary element for some plants and animals, high concentrations of copper in water can be toxic to fish and other aquatic species.

Several treatment methods are used to remove these pollutants from wastewater, such as precipitation, ion-exchange, evaporation, oxidation and membrane filtration [2–4]. However, application of such technologies is restricted because of technical or economical limitations [4–7]. Biosorption as an alternative and effective technology has been widely studied over recent years, because of its wide range of target pollutants, high sorption capacity, excellent performance, ecofriendly nature and low operating cost [8,9]. The term, biosorption is used to describe a method that utilizes materials of biological origin (biosorbents formulated from non living biomass) for the removal of target substances from aqueous solutions [10,11]. Compared with traditional technologies, biosorption has advantages such as technically feasible and use of cheap material as biosorbents.

A literature review showed that agricultural wastes [12–20] are frequently used as biosorbent to removal of heavy metals in monometallic system. However, although the biosorption of single metal ions to various agricultural wastes has been extensively studied and biosorption isotherms have been developed for single metal ion situations, very little attention has been given to the biosorption of multi-metal ions systems. Nevertheless, as it is very improbable to have just one metal species in solution, recent research studies have been extended to systems concerning two or more metals [21–27]. These studies have focused on the effect of a given metal on the sorption uptake of another one by a certain biomass and on the relative affinity of the biomass for each metal.

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In this way, the evaluation, interpretation and representation of multimetallic systems is more complex than of monometallic systems because of competition phenomena between metals in solution for the biomass active sites [28–30]. These competition phenomena, in turn, depend on factors such as metal speciation, solution pH, nature of bond sites, metal concentration or selectivity of the biomass to metal species.

Recent studies on biosorption have shown that almond shell can be used as potential biosorbent for the removal of heavy metals [31–33]. All these studies have evaluated almond shell in single metal batch systems. However, the aim of the present study is to evaluate competitive sorption of copper and lead by almond shell in binary metal mixture and compare it with a single metal ion situation in batch and continuous systems.

2. Materials and methods

2.1. Almond shell

The almond shell used in the present study is a subproduct from peeled of almonds, supplied by Carsan Biocombustibles S.L. factory from Granada (Spain). Particles of almond shell were milled with an analytical mill (IKA MF-10) and <1 mm fraction was chosen for the biosorption tests without any pre-treatment. A summary of the properties of the biosorbent that were discussed on a previous work are listed in Table 1 [33].

2.2. Metal solutions

Stock solutions of 1000 mg/L for Pb(II) and Cu(II) were prepared, by dissolving desired amount of $Pb(NO_3)_2$ and $Cu(NO_3)_2 \cdot 3H_2O$ in 500 mL of distilled water. After, rest of solutions of different concentrations was prepared by appropriate dilution of both above stock solutions.

2.3. Experimental procedure

The biosorption tests were performed by batch and continuous techniques in monometallic and bimetallic systems.

Table 1
Physico-chemical characterization of almond shell.

Physical characterization	
BET surface area	0.406 m^2/g
Pore volume	0.918 cm^3/g
Pore diameter	54.5 Å
Particle size	<1 mm
Potentiometric titrations	
Total concentration of acid–basic sites	0.592 mmol/g
Concentration of carboxylic group	0.309 mmol/g
pH_{pzc}	6.06
Elemental analysis	
Carbon	44.77%
Hydrogen	7.10%
Nitrogen	0.43%
Sulphur	0.05%
Oxygen	47.65%
FTIR analysis	
Wavenumbers (cm^{-1})	Group
3330	O–H
2922	C–H
1727	C=O
1506	C=C
1250	C–O
1030	C–O alcoholic
897 and 667	C–H_n aliphatic or aromatic

2.4. Bach experiments

The adsorption experiments were conducted in a batch system with a 150 mL flask in a thermostatic shaker at 25 °C. The experiments were performed by mixing 1 g of biomass in 100 mL of metal solutions at different concentrations of Pb(II) and Cu(II) respectively. The pH is initially adjusted to 5 and it is kept constant in this value with 0.1 mg/L HCl and 0.1 mg/L NaOH solutions. After 120 min the final Pb(II) and Cu(II) concentrations were measured by atomic absorption spectrometry (Perkin-Elmer Model AAnalyst 200). Previous studies showed that the equilibrium of the process is reached at this contact time [34]. In order to analyze the biosorption equilibrium of copper in binary systems Cu(II)–Pb(II), we performed experiments changing initial copper concentration from 10 to 300 mg/L and for three initial lead concentrations (20, 50, and 100 mg/L).

2.5. Column experiments

The continuous-flow sorption experiments were conducted in a jacket glass column with an internal diameter of 1.5 cm and a length of 23 cm packed with almond shell particles. To enable a uniform inlet flow of the solution into the column, glass beads of 5 mm diameter were placed in the bottom of the column. Glass beads are not mixed with adsorbent.

The bed density and porosity of almond shell are approximately 0.564 g/cm^3 and 54.5%, respectively, and the empty bed contact time 57 s. The feed solution and the fixed-bed column temperature were maintained at 25 °C with a thermostatic bath. Lead and copper solutions at known concentration (this concentration is the desired one in each experiment) were pumped through the column of sorbent using a peristaltic pump (Dinko model D21V) at different flow rates. Samples from the column effluent were collected at regular intervals and the final Pb(II) and Cu(II) concentrations were analyzed by atomic absorption spectrometry (Perkin-Elmer Model AAnalyst 200). The column studies were performed at pH 5 (this value was considered the optimum for the biosorption process in previous studies [34]), and the effluent pH was permanently recorded.

3. Results and discussion

Characterization of almond shell is vital to understanding the metal binding mechanism onto biomass. The physicochemical characteristics of the almond shell are shown in Table 1. With respect to physical properties, almond shell show a high BET surface area (0.406 m^2/g) and high pore volume (0.918 cm^3/g). About the potentiometric titrations, almond shell showed a high total concentration of acid–basic sites, assuming an acid character with a pH_{pzc} value of 6.06. Elemental analysis results show that almond shell was composed of 44.77% carbon, 7.10% hydrogen, 0.43% nitrogen, and 47.65% oxygen. Finally, the FTIR analysis showed the presence of carboxyl and hydroxyl groups characteristic of these types of waste. These physico-chemical properties (high surface area, high total concentration of acid–basic sites, the presence of some characteristic groups, *etc.*) make that almond shell was a good biosorbent [31].

3.1. Biosorption of mixture Cu(II)–Pb(II) in a batch system

3.1.1. Mathematical background

One of the difficulties in studying the adsorption of metal ions from wastewaters is the presence of a multitude of metals. When in the aquatic system there are more of one metal, may occur a competition between metals. So that, the evaluation, interpretation and representation of results is more complex than in single