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Experimental binding of lead to a low cost on biosorbent: Nopal (*Opuntia streptacantha*)

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Abstract

The use of nopal cladodes (*Opuntia streptacantha*) as raw material for Pb²⁺ biosorption was investigated. Batch experiments were carried out to determine Pb²⁺ sorption capacity and the efficiency of the sorption process under different pH, initial Pb²⁺ and nopal biomass concentrations. The experimental data showed a good fit to Langmuir and Freundlich isotherms models. The maximum adsorption capacity for Pb²⁺ was 0.14 mmol g⁻¹ with an efficiency higher than 94% (pH 5.0 and 2.5 g L⁻¹ nopal biomass). The Pb²⁺ kinetics were best described by the pseudo-second-order rate model. The rate constant, the initial sorption rate and the equilibrium sorption capacity were determined. The practical implication of this study is the development of an effective and economic technology in which the nopal biomass did not undergo any chemical or physical pretreatment, which added to nopal abundance in Mexico and its low cost makes it a good option for Pb²⁺ removal from contaminated waters.

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1. Introduction

The use of low-cost adsorbents as a replacement for costly methods of removing heavy metals from solution has increased during the last years. Common materials used are fly ash, zeolite, peat, chitosan, waste slurry, lignin, seaweed, etc (Bailey et al., 1999; Babel and Kurniawan, 2003).

In this study, we investigated the technical feasibility of nopal cladodes (*Opuntia streptacantha*) as a low-cost heavy metal (Pb²⁺) adsorbent. In Mexico, fresh weight nopal production is about 600,000 tons year⁻¹ (Flores, 1997). Furthermore, there are about 3 million ha of wild nopal (www.sagarpa.gov.mx; www.inegi.gov.mx). Nopal abundance makes it a good low-cost candidate for industrial utilization, principally if it requires little processing. In a general way, technical applicability and cost-effectiveness are the key factors when selecting a heavy metal adsorbent

for treatment of contaminated waters. Due to their low cost, these materials can be disposed without expensive regeneration, after they have been used.

The cactus cladodes contains, when cut, a polysaccharide mucilage, characteristic of members of the Cactaceae family (Nobel et al., 1992) that does not gel in the presence of calcium. The carbohydrate composition of mucilage from several *Opuntia* species has been well characterized (Amin et al., 1970; Trachtenberg and Mayer, 1981; McGarvie and Parolis, 1981; Matsuhiro et al., 2006). In general, the *Opuntia* sp. cladodes mucilage contains varying proportions of D-galactose, L-arabinose (pyranose and furanose forms), D-xylose, and L-rhamnose as well as D-galacturonic acid. Their chemical composition reveals close resemblance with pectins, structural elements of primary cell walls and intercellular regions of higher plants. Mucilage content in dry weight of *O. streptacantha* has been reported as 2.21% (Goycoolea and Cárdenas, 2003).

Taking advantage of the cladodes properties, nopal mucilage is used in culinary applications, as an additive for food industry, for improving stability and compressibility

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of building materials, for cosmetic applications, for improving house paint as an adhesive for lime, as a flocculant agent for water purification, and other uses (Sáenz et al., 2004) and in traditional treatments of diabetes, gastritis, hyperglycemia, etc (Stintzing and Carle, 2005). Nevertheless, there are very few studies on the use of nopal for heavy metal removal from aqueous solutions. Barrera-Diaz et al. (2005) compared the effectiveness of a zeolite and nopal in Cd and Pb removal from contaminated waters, but they used the nopal ectodermis, not the entire nopal cladodes.

The aim of the present study is the use of nopal (*O. streptacantha*) cladodes biomass as raw material for heavy metal (Pb²⁺) biosorption from solution. The mechanism of Pb uptake from contaminated solutions is investigated through equilibrium and kinetic experiments under different pH, initial metal and nopal biomass concentrations.

2. Methods

2.1. Materials

Nopal plants were collected from Silao (Estado de Guanajuato, México), washed with deionised water to remove dirt, dried at 60 °C for 24 h, crushed, milled and sieved through a 0.5 mm sieve (N° 35 mesh). The nopal biomass cation exchange capacity (CEC) (meq g $^{-1}$) was determined by titration with 0.1 M NaOH on the nopal acidic form, the latter being obtained by stirring 10 g L $^{-1}$ of nopal biomass in an aqueous solution of 0.01 M HCl overnight, then washing with ultrapure water and drying at 60 °C.

All chemicals used were of analytical-reagent grade. Ultrapure quality deionised water (Nanopure, Infinity, Dubuque, Iowa, USA) was used throughout. Pb²⁺ solutions were prepared by dilution of 1000 mg L⁻¹ PE Pure Standard (Perkin–Elmer, Norwalk, USA). HNO₃ and NaOH (J.T. Baker, Xalostoc, Mexico) solutions (0.01 M) were prepared by dilution of concentrated acid and base. All the glassware used for dilution, storage and experiments was cleaned with Extran detergent, thoroughly rinsed with tap water, soaked overnight in a 20% HNO₃ solution and finally rinsed with ultrapure quality water before use.

2.2. Equilibrium adsorption studies

Batch equilibrium tests were conducted by suspending the nopal biomass (0.10, 0.20 and 0.30 g) in the Pb^{2+} metal solution (40.0 mL) for 120 min in a rotary shaker at 140 rpm. Preliminary experiments of adsorption kinetics indicated that a period of 120 min was sufficient to attain equilibrium. At the end of the agitation period, samples were centrifuged at 3000 rpm for 5 min and then filtered using 0.45 μ m cellulose acetate membrane (Micro Separations Inc., MSI, Westboro, MA, USA). Different initial metal concentrations were used (from 0.048 up to 0.241 mM). The experiments were performed at different

pH (3.0, 4.0, 5.0 and 6.0). The initial and final concentration of Pb²⁺in the water solution was determined and also the initial and final pH. Blanks were performed under the same conditions but in the absence of metals.

The amount of metal adsorbed Q_e (mmol g^{-1}) was calculated according to

$$Q_{\rm e} = (C_0 - C_{\rm e})V/W,\tag{1}$$

where C_0 (mM) is the initial Pb²⁺ concentration, C_e (mM) is the equilibrium concentration after the adsorption has taken place, W is the dried nopal biomass (g) and V the solution volume (mL).

The efficiency of biosorption (%) was calculated using

$$\% = (C_0 - C_e)100/C_0. \tag{2}$$

2.3. Kinetic studies

The experiments were carried out by suspending nopal biomass (0.100 g) in 40.0 ml of 0.048, 0.097, 0.145, and 0.245 mM solutions of Pb²⁺ for 0, 1.0, 7.0, 37.0, 78.0, 120.0 and 184.0 min, as explained before. All the results obtained in the experiments were corrected from blanks performed under the same conditions but in the absence of biosorbents species. All results obtained represent the average from two replicate experiments.

2.4. Instrumentation

Pb²⁺, Ca²⁺ and K⁺ concentration were determined by flame atomic absorption spectrophotometry (FAAS) (Perkin–Elmer, Aanalyst 300, Shelton, USA) according to standard methods (American Public Health Association APHA, 1993). All determinations were performed in triplicate with a relative error <1.0% for all measurements.

3. Results and discussion

3.1. Cation exchange capacity

The estimation of the CEC, that corresponds to the total number of ionic sites per nopal gram, is essential to the selection of biosorbents than can be used in the treatment of metal contaminated waters. The potentiometric titration of the protonated biomass showed the typical shape attributed to the carboxylic groups of polygalacturonic acid residues in the mucilage backbone (Fig. 1) with only one flexion point, corresponding to pK_a values ca 3.5. It has been reported that pectins do not have a well-defined dissociation constant. Apparent pectin pK_a values of 3-4 have been reported (Deuel and Stutz, 1958). Analysis of the curve showed that the cation exchange capacity was 0.57 meg g⁻¹ of dry nopal, close to the CEC value of the acid form of sugar-beet pulp (CEC = 0.55 meg g^{-1}) (Dronnet et al., 1997), as pectic substances account for more than 40% of the dry matter of the beet pulp.

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