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Optimization of the continuous biosorption of copper with sugar-beet pectin gels

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A B S T R A C T

Sugar-beet pectin xerogels obtained from residues of the sugar industry are an adequate material for metal recovery from effluents in continuous systems. The xerogels were used as a biosorbent for copper removal in a fixed-bed column. The performance of the system was evaluated in different experimental conditions: flow rate, bed height, inlet metal concentration and feeding system (drop and reverse). The effect on the biosorption parameters (saturation time, amount of adsorbed and treated metal, column performance and metal uptake) and the shape of the breakthrough curves was determined. The saturation time increased with increasing bed height but decreased with increasing feed flow rate and inlet metal concentration. Preferential flow channels greatly influenced the metal uptake and column performance. Copper was completely desorbed with 0.1 M HNO_3. Additionally, the column data fitted both the linear and nonlinear expressions of the Thomas model.

1. Introduction

The treatment of highly dilute heavy metal effluents is becoming an environmental and sanitary issue due in part to increasingly restrictive regulations. In this way, conventional technologies such as chemical precipitation and filtration, electrochemical treatments, reverse osmosis, ion exchange, adsorption and evaporation can be costly. Biosorption is a simple alternative based on the passive binding of metals or other compounds on the chemically active sites or functional groups of a certain biosorbent (biomass) by chemical and physical processes such as ion exchange, complexation and microprecipitation (Volesky, 2003). Furthermore, biosorbents can be obtained from residual and/or inexpensive materials (Dermirbas, 2008). In industrial applications, continuous biosorption systems, such as fixed and fluidized beds and total mix reactors, can treat large amounts of effluent.

Fixed beds are the simplest and the most effective configuration in the use of biomass and the recovery of metals from solutions (Volesky, 2003). In these systems, the metal solution is either drop-fed from the top or reverse-fed from the bottom of a biomass column creating a mass transfer or exchange zone in which biosorption occurs. A saturation front advances gradually from the entrance to the exit of the column. At this point there is an increase in the outlet metal concentration (C) until it equals the inlet concentration (C_0) producing an inflection in the elution curve.

The breakthrough curve provides information about the biosorption parameters of the fixed-bed system and represents the exit metal concentration (expressed as a dimensionless number, C/C_0) vs. time. Theoretical models can be used to predict these curves as a way to scale-up the process for industrial applications. Among these, the Thomas model is widely used to describe the biosorption behavior of fixed-bed columns (Padmesh et al., 2005; Vigayaraghavan et al., 2005; Han et al., 2006).

The breakthrough point, defined as the time at which the outlet concentration reaches a predefined limit, determines column service time. This concentration is chosen according to the decontamination goal or the limit given by legal regulations. Even though the column is not completely saturated, it can be disposed or desorbed for the recovery of the adsorbed metal.

Biomass in its native state is generally inadequate for fixed-bed systems due to its small particle size, low density, and lack of mechanical resistance. Xerogels overcome these problems by providing a uniform size and enough strength of the biosorbent that can be easily separated from the treated solutions in fixed-bed operations. Characteristics such as bead size, porosity and permeability can be modulated when preparing the biosorbent to suit the

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requirements of the biosorption system for large scale use. This is not always possible or very difficult with native biomass since they may suffer compaction due to their irregularity.

Sugar-beet pectin xerogels can be an interesting alternative to more widely used alginate, obtained from readily abundant brown algae, in continuous biosorption applications (Papageorgiou et al., 2008; Mata et al., 2008). Pectins, like alginate, are rich in carboxyl groups that can attract metal cations due to their negative charge. These functional groups have been described as the main groups involved in the biosorption process (Volesky, 2003; Mehta and Gaur, 2005).

Sugar-beet pectins are obtained from pulp residues of the sugar industry. In Spain, that industry generates more than 200,000 tons of pulp per year that is sold at low price as animal feed. They cannot be used in the food industry due to their high content of neutral sugars and low level of galacturonic acid (<65%) (May, 1990). Nevertheless, unlike other types of pectins, such as apple and citrus, the raw material is already dry and seasonal independent. Several previous studies have characterized the sorption properties of sugar-beet pulp in batch systems (Reddad et al., 2002; Aksu and İşoğlu, 2005). Therefore, this residual and inexpensive material could be an excellent source of pectins as biosorbent and immobilizing agent.

Sugar-beet pectin xerogel is a byproduct of the pulp with biosorbent characteristics completely different. Adsorption performance depends on the metal adsorbed, biosorbent characteristics and experimental conditions. Due to the lack of uniformity in the experimental procedures used in the literature, the comparison between different biosorbents can be a challenging task. Thus, preliminary studies in batch systems using cadmium, lead and copper solutions were performed under similar experimental conditions in order to compare sugar-beet pulp, sugar-beet pectin hydro and xerogels, and alginate xerogels (Mata, 2006). Langmuir parameters (maximum uptake and affinity constant) obtained from these studies showed that sugar-beet pectin xerogels have the lowest copper uptake with respect to other materials (Fig. 1). The copper affinity constant of pectin hydro and xerogels was higher than for alginate xerogels and pulp. Therefore, copper was the metal chosen to investigate the effect of different operating conditions in column biosorption studies.

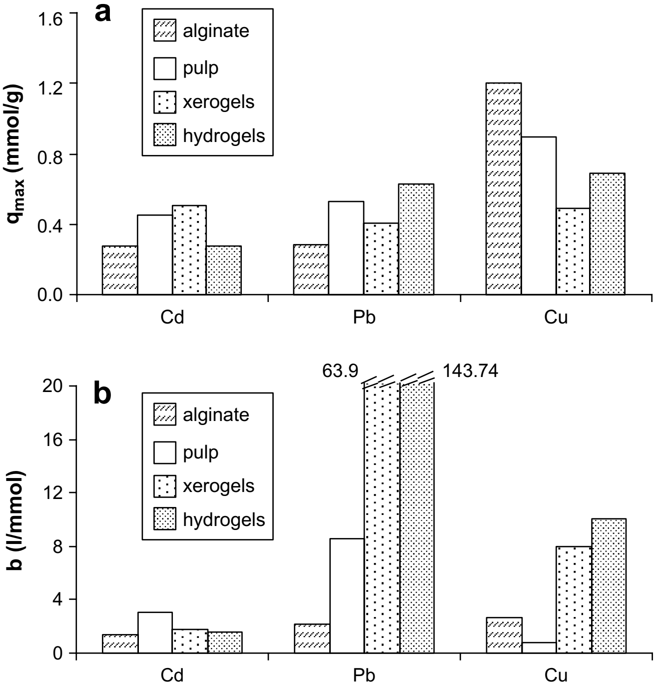

Fig. 1. Langmuir parameters of alginate xerogels, sugar-beet pulp, and sugar-beet pectin hydro and xerogels: maximum metal uptake (q_{max}) and affinity constant (b) (Mata, 2006).

There are only two previous works dealing with batch metal binding with sugar-beet pectins but none of them addresses continuous biosorption (Dronnet et al., 1996; Harel et al., 1998). In this study, the copper biosorption behavior of sugar-beet pectin xerogel columns was evaluated by operating under different experimental conditions: feed flow rate, bed height (amount of biosorbent) and inlet metal concentration. The experimental data were used to determine the optimum experimental conditions that yielded the most favorable breakthrough curves and highest metal uptakes for this metal. Additionally, the Thomas model parameters were calculated and compared with the experimental results. This work constitutes a preliminary step for the industrial application of sugar-beet pectins in the decontamination of dilute metal effluents.

2. Experimental

2.1. Pectin xerogels

The pectin was extracted from a sugar-beet pulp using 0.3 M H_2SO_4 at 80 °C and demethylated with 1 M NH_3 at 4 °C following the method described by Harel et al. (1998) (Mata, 2006). The hydrogel beads were obtained by dropping a 1.5% pectin suspension into a cooled 1 M $CaCl_2$ solution, kept at 4 °C overnight and the excess $CaCl_2$ rinsed with distilled water. The hydrogel beads measured approximately 3 mm of diameter and had an average weight of 3.33×10^{-2} g. The beads were air dried at room temperature to obtain xerogels of approximately 1.3 mm diameter and an average weight of 1.11×10^{-3} g (30 times lighter than the original hydrogels). Xerogels contained approximately 73% of pectin and 27% of calcium.

2.2. Continuous biosorption and desorption

Biosorption tests were performed at room temperature (23 ± 1 °C) in glass columns (1 cm inner diameter and 32 cm length) packed with sugar-beet pectin xerogels. The experiments were carried out with monometallic solutions prepared from stock solutions of 1000 mg/l of Cu^{2+} as $CuSO_4.5H_2O$ of analytical grade. The initial pH value of the metal solution (5.0) was adjusted with dilute H_2SO_4 and NaOH. That pH gave the maximum metal uptakes in previous batch studies with sugar-beet pectin xerogels and besides it is below the precipitation pH at the metal concentration used (Mata, 2006). The metal solutions were fed either from the top of the columns in the drop-fed system or from the bottom of the columns in the reverse-fed system using a peristaltic pump (Watson Marlow model 303). Glass wool was placed on top and bottom of the column to ensure a good distribution of solution and to prevent the loss of biomass. Effluent samples were collected regularly and analyzed by AAS in a Perkin Elmer 1100B Atomic Absorption Spectrometer until the columns were exhausted, that is, when the inlet and outlet metal concentrations were the same. Once the optimum conditions were determined, metal loaded biomass was desorbed using 0.1 M HNO_3 for 24 h or until the outlet metal concentration remained constant and equal or close to zero.

Continuous biosorption parameters were calculated from the breakthrough curves of the columns. The amount of metal passing through the column (Me_{tr}) and that retained or adsorbed within the column (Me_{ad}) can be determined from the plot of $(1 - C/C_0)$ vs. time as follows: