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Studies on sorption, desorption, regeneration and reuse of sugar-beet pectin gels for heavy metal removal

Y.N. Mata, M.L. Blázquez*, A. Ballester, F. González, J.A. Muñoz

Department of Materials Science and Metallurgical Engineering, Complutense University of Madrid, Ciudad Universitaria s/n 28040 Madrid, Spain

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ABSTRACT

This work reports the effectiveness of sugar-beet pectin xerogels for the removal of heavy metals (cadmium, lead and copper) after multiple batch sorption–desorption cycles, with and without a gels regeneration step. Metals were recovered from xerogel beads without destroying their sorption capability and the beads were successfully reused (nine cycles) without significant loss in both biosorption capacity and biosorbent mass. Metals uptake levelled off or increased after using a 1 M $CaCl_2$ regeneration step after each desorption. Calcium, as a regenerating agent, increased the stability and reusability of the gels repairing the damage caused by the acid and removing the excess protons after each elution providing new binding sites. Because of their excellent reusability, pectin xerogels are suitable for metal remediation technologies.

1. Introduction

The treatment of effluents charged with highly dilute heavy metal concentrations is becoming an important issue because of environmental and sanitary problems, and increasingly restrictive legislations. Such effluents pose serious problems for the industry due to the high cost of metal decontamination using conventional technologies. Biosorption is a cost effective alternative for the purification of effluents containing low metal concentrations. Certain types of biomass (biosorbents) can passively bind metals and other pollutants such as dyes or organic compounds on chemically active sites or functional groups [1].

Different materials under different conditions have different metal uptake capacities and metal affinities. Recently, attention has been focused on byproducts or wastes of biological origin produced in large scale industrial or agricultural operations [2]. These biomass are characterized by their availability, high efficiency, easy handling and low cost. Among these, sugar-beet pulp (obtained from *Beta vulgaris*), a residue from the sugar industry has shown biosorption potential [3]. Moreover, biomass in its native state is generally inconvenient for biosorption applications due to its small particle size, low density, and lack of mechanical resistance. In this way, xerogels made from sugar-beet pectins extracted from the pulp are an interesting alternative.

Compared to other pectins obtained from other sources, like citrus, apple and sunflower pectins, sugar-beet pectins have the advantage that the raw material is already dried and does not depend on seasonality. There are previous studies characterizing sugar-beet pectin xerogels as a biosorbent [4]. Furthermore, cost reduction for industrial applications of a biosorption system requires that the biosorbent has an adequate mechanical stability, permeability and metal uptake in a series of sorption–biosorption cycles. In previous experiments, xerogel pectin beads have shown adequate stability at different solution pH and stirring conditions [4].

Once the biosorbent is exhausted, the metal-loaded biomass is in the form of residual muds. A decision has to be taken about the priority of removing a polluting or toxic substance from effluents and/or water that could be used for drinking or agricultural purposes, and about the problems that arise from the handling of exhausted biomass from the biosorption process. In this sense, desorption and reutilization of the biosorbents in adsorption–desorption cycles could help in reducing these residues. Desorption can be carried out by proton exchange using acids, chelating agents (EDTA) or exchange with other ions (i.e. $CaCl_2$) [5,6]. An efficient eluant is one that desorbs the metal completely without deteriorating the biomass. After elution, a metal concentrated solution is obtained from which metals can be recovered using electrochemical or other conventional techniques. In the case of cadmium, lead and copper desorption from sugar-beet pectin xerogels, previous studies have shown that HNO_3 is more effective than other inorganic acids (HCl or H_2SO_4) [4].

* Corresponding author. Tel.: +34 91 3944335; fax: +34 91 3944357.
E-mail address: mlblazquez@quim.ucm.es (M.L. Blázquez).

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After metal desorption with acids, a regeneration step can be used to prevent biomass deterioration or loss of biosorption capacity. The choice of regenerating agent depends on the kind of biosorbent used and the metals adsorbed which determines the type of metal ion interaction with the solid material. In some cases, a simple wash with distilled water has been used [6,7]. In the present study the regeneration step of the biosorbent was carried out with the original gelling solution of the sugar-beet pectin gels, 1 M $CaCl_2$.

The aim of this work was to determine the effectiveness and resistance of sugar-beet pectin gels for the removal of Cd^{2+}, Pb^{2+} and Cu^{2+} from aqueous solutions in various batch adsorption–desorption cycles using 0.1 M HNO_3 as an eluant and with and without a 1 M $CaCl_2$ regeneration step. Published studies on metal binding with sugar-beet pectins are scarce and even less with calcium gels [4,8–10]. Studies concerning desorption, reuse and regeneration of metal-loaded biosorbents are also very rare and none of them addresses the use of pectins or their gels [11,12]. In recent reviews, Sud et al. [2] and Wang and Chen [13] pointed out that further research is needed in areas of metal desorption and biosorbent regeneration.

2. Materials and methods

2.1. Biosorbents

Azucarera Ebro Agrícola provided the sugar-beet pulp from the Toro plant in Zamora, Spain. The pulp was collected directly from the final drying line to ensure freshness. Sugar-beet pectin was extracted following the protocol proposed by Harel et al. [9]. The sugar-beet pulp was repeatedly washed with tap water and filtered with cheesecloth to remove the molasses. After that, a 5% pulp suspension in 0.3 M H_2SO_4 was heated during 4 h at 80 °C in a water bath. The solids were filtered and a solution of 95% ethanol was added to the remaining liquid causing pectin precipitation. The pectin was filtered and washed repeatedly with different ethanol solutions: twice with 70% ethanol and once with 85% and 95% ethanol successively. The remaining solid was dried in a stove at 35 °C and ground with an agate mortar.

The product of the extraction process, a highly methoxyl pectin, was demethylated in order to enable calcium gelation to produce adequate gels as described in a previous publication [4]. The demethylation method was adapted from the methods proposed by Harel et al. [9] and Le Cerf et al. [14]. A solution of 2% pectin in deionized water was stirred for at least 2 h, precipitated with 95% ethanol and filtered with cheesecloth. The pectin was cooled to 4 °C and a solution of 1 M NH_3 at the same temperature was added until a 2% pectin solution was obtained. This solution was stirred until homogenization and kept 12 h without stirring at 4 °C. Then, it was precipitated with a 70% ethanol solution, filtered and washed again twice with the ethanol solution. After three filtrations, it was kept stirred for 6 h in the 70% ethanol solution. Finally, it was filtered and resuspended in a 85% and then a 95% ethanol solutions. The remaining solid was dried in a stove at 35 °C and ground with an agate mortar.

The pectin gel beads were prepared by dropping a 1.5% pectin aqueous solution into a cooled 1 M $CaCl_2$ solution. The viscous solution was pressed through a syringe (internal diameter of 0.5 mm) to ensure bead uniformity. The beads were kept at 4 °C for at least 24 h in the same solution. The excess $CaCl_2$ was rinsed with distilled water. The hydrogel beads obtained had a diameter of 3 ± 0.2 mm and an average weight of 3.33×10^{-2} g. The beads were air dried at room temperature (23 ± 1 °C) to obtain xerogel beads of approximately 1.4 ± 0.2 mm of diameter and 1.11×10^{-3} g of weight (30 times lighter than the original hydrogels). On average, 1 mg of pectin yields 40 mg of hydrogels or 1.33 mg of xerogels. Xerogels contained approximately 73% of pectin and 27% of calcium.

2.2. Biosorption experiments

Biosorption experiments were carried out at room temperature (23 ± 1 °C) with monometallic 100 mg/l solutions (Cd^{2+}, Pb^{2+}, and Cu^{2+}) prepared from 1000 mg/l stock solutions using chemical reagents of analytical grade: $CdSO_4 \cdot 8/3H_2O$, $Pb(NO_3)_2$ and $CuSO_4 \cdot 5H_2O$. In the case of lead, nitrate instead of sulfate was used to avoid metal precipitation. Previous studies have shown that the effect of this anion is negligible [15]. The initial pH value of the metal solutions was adjusted with 1 M H_2SO_4 for Cd and Cu, 1 M HNO_3 for Pb, and 1 M NaOH as needed and based on previous optimum pH studies for the greatest metal binding capacity: pH 6 for Cd, 4 for Pb and 5 for Cu [4]. Special care was taken to select values below each metal's hydroxide precipitation pH for the metal concentrations used in this study, to ensure that metal uptake was only due to biosorption and not to chemical precipitation. The xerogel beads (0.05 g) were put in contact with the metal solutions (50 ml, 1 g/l biosorbent concentration) and liquid samples were removed at different times (0, 15, 60, 120, 240, 480 and 1400 min) for AAS analysis (PerkinElmer 1100B Flame Atomic Absorption Spectrometer) to ensure equilibrium concentration was reached in each biosorption. All the experiments were performed in duplicate and each point is the average mean of both results.

The amount of metal ions adsorbed per gram of biomass (q_e, mmol/g of pectin) was obtained as follows:

$$q_e = \frac{C_o - C_e}{B} \quad (1)$$

where C_o is the initial metal concentration (mmol/l); C_e is the equilibrium (final) metal concentration (mmol/l); B is the biomass concentration (g/l).

2.3. Metal desorption and biosorbent regeneration

After adsorption, the metal-loaded gels were filtered, weighed and placed in contact with a 0.1 M HNO_3 desorption solution at a biosorbent concentration of 1 g/l. This acid was chosen from previous experiments as an effective eluant of cadmium, lead and copper from sugar-beet pectin gels [4]. Metal concentration was determined in samples removed at 2, 5, 10, 30 and 60 min to ensure that the equilibrium concentration had been reached in order to calculate the overall metal uptake in each cycle. In order to determine the reusability of pectin gels, the same beads were used in consecutive adsorption–desorption or adsorption–desorption–regeneration cycles. In each cycle, the xerogels were filtered and repeatedly washed with deionized water after each desorption to eliminate the excess of acid. In the regeneration step, the gels were soaked in a 1 M $CaCl_2$ solution for 12 h at 4 °C, filtered, and washed with deionized water before being reused in a new sorption–desorption cycle. The experimental set up for the adsorption–desorption–regeneration cycles is depicted in Fig. 1.

The stability of the xerogels was controlled by weighing the gels after filtration at the end of each cycle. Since xerogels were weighed prior drying, the calculation of the metal uptake capacity after each cycle was made taking into account the initial amount of biosorbent, that is, without considering possible biomass losses. In this way, heat and desiccation during the dehydration process would constitute an additional pre-treatment procedure that could alter the xerogel characteristics in the next biosorption–desorption cycle, adding an unnecessary step that would make the process less feasible.