Chemical Engineering Journal 150 (2009) 289–301

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Sugar-beet pulp pectin gels as biosorbent for heavy metals: Preparation and determination of biosorption and desorption characteristics

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ARTICLE INFO

Article history:
Received 28 February 2008
Received in revised form 16 December 2008
Accepted 5 January 2009

Keywords:
Sugar-beet
Beta vulgaris
Pectin
Biosorption
Desorption
Heavy metals

ABSTRACT

The present work reports the feasibility of using sugar-beet pectin gels for the removal of heavy metals from aqueous solutions. Sugar-beet pectin hydro- and xerogels were tested in the batch biosorption and desorption of cadmium, lead and copper. Pectins were successfully extracted and demethylated from the sugar-beet pulp, an agricultural residue, and gelled in the presence of $CaCl_2$. The stability of the hydro- and xerogel pectin beads made them suitable for biosorption of heavy metals in different conditions. Biosorption data were fitted to the pseudo-second order kinetic model and the Langmuir isotherm model, obtaining the corresponding parameters. Treated and untreated beads were characterized using FTIR and SEM to determine possible binding mechanisms. The main mechanisms involved were ion exchange with calcium of gel structure and chelation or complexation with carboxyl groups. After biosorption, calcium in the gels was substituted by metal cations reorganizing the structure of the gel matrix in a way that was visible using scanning electron microscopy. HNO_3 0.1 M was the best eluant for the reutilization of the gels and recovered all the adsorbed metal unlike HCl and H_2SO_4. Sugar-beet pectins could be used as an efficient biosorbent for the treatment and recovery of Cu, Pb and Cd from wastewater.

1. Introduction

Heavy metals are highly recalcitrant elements with a high potential to pollute water resources that can be accumulated and concentrated in living tissues along the food chain. Copper, lead and especially cadmium are a sanitary and ecological threat, even at very low concentrations. The recovery of these metals from effluents not only ensures that they do not reach the environment but also help to preserve natural resources. Furthermore, in the case of copper, the steadily increasing market price is another incentive for a profitable recovery.

Traditional methods for recovering heavy metals from effluents are generally expensive or inadequate to treat highly diluted effluents. These methods include: chemical precipitation and filtration, redox reactions, electrochemical treatments, reverse osmosis, ion exchange, adsorption and evaporation. Biosorption is a cost effective alternative that can be appropriate in the purification of effluents with low metal concentrations and can also be used to remove other pollutants such as dyes or organic compounds. It is a property of certain types of organic matter or biomass (biosorbents) to passively bind metals on chemically active sites or functional groups [1]. The type of biomass used determines the metal uptake and the selectivity of the recovery process. The use of dead biomass makes the process nutrient-independent, faster and increases the metal uptake [2].

Different models can describe the biosorption kinetics, such as the pseudo-first order model proposed by Lagergren and the pseudo-second order model proposed by Ho and McKay [3]. The maximum metal uptake and the affinity of the biomass for a certain metal can be obtained from the sorption isotherms. Although there are different isotherm models, the Langmuir model is, by far, the most used in simple systems.

Recently attention has been addressed towards byproducts or wastes from large scale industrial operations and agricultural waste materials based on their availability, high efficiency, easy handling and low cost [4]. Sugar-beet (*Beta vulgaris* L.) pectins can be obtained from sugar-beet pulp, a residue of the sugar processing industry. 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 stationality. Sugar-beet pulp is sold as animal feed at very low prices and is readily available for revalorization. Just in Spain more than 200,000 tons are generated per year (Grupo Ebro Puleva). Sugar-beet pulp has a high pectin content (15–30%), but these pectins have poor gelling properties compared to citrus and apple pectins due to their high degree of methylation and low molecular weight. Moreover, sugar-beet pectins have not been extensively used in traditional applications in the food industry,

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doi:10.1016/j.cej.2009.01.001

mainly because of their high neutral sugar and low galacturonic acid content [5]. Therefore, the development of alternative applications for these pectins, such as biomass immobilization and the biosorption of heavy and precious metals, is highly desirable.

Pectins are polysaccharides of the middle lamella and primary cell wall in which they are crosslinked with cellulose and hemicellulose fibers. The structure of pectin is complex and can vary depending on the source and the extraction method. It is a polysaccharide composed of galacturonic acid units with α(1,4) bonds, which constitute the "smooth regions". In the "hairy regions", the rhamnose units in the carbon skeleton are branched with secondary chains, mainly arabinans, normally lost during extraction. Other residues are: methanol, acetic acid, phenolic acid, and amides. Ferulic acid is a characteristic group of sugar-beet pectins. Therefore, the main functional groups of pectin are: hydroxyl, carboxyl, amide and methoxyl. These functional groups have been traditionally associated to heavy metal binding, especially carboxyl groups with a great biosorption and heavy metal removal potential [1]. Additionally, pectins in granulated form such as gel beads can be used for continuous applications such as fixed-bed columns. This makes sugar-beet pectins an interesting alternative to similar polysaccharides such as alginate that are already widely used and accepted.

Most of the pectins present in the sugar-beet pulp are high methoxyl and have more than 50% of methoxylated residues. They gel at low pH values and in the presence of a high concentration of soluble solids. The resulting gels dissolve quickly in water and have a soft consistency and therefore have no application in the biosorption of metals or in the immobilization of biomass. Low-methoxyl pectins have less than 50% of methoxylated residues and can be obtained from high-methoxyl pectins by demethylation. These pectins are sensitive to gelation with divalent cations such as calcium according to the "egg-box model" proposed by Rees but methoxyl groups are an impediment for the formation of the calcium bridges [6]. Their gels are stable in aqueous solutions and can be used in similar applications like those of alginate including biomass immobilization and heavy and precious metal biosorption, among others [7].

Demethylation occurs at low temperatures and in an alkaline media through a base-hydrolysis of the esther groups (saponification) [5,8]. At neutral or alkaline pH values pectin degradation takes place by the β-elimination of the glycosidic bond that is adjacent to the esterified units of the galacturonic acid. The degradation increases with temperature and is parallel to the demethylation process. Different types of pectin demethylation methods can be used: acid, alkali, ammonia and enzyme treatments [8]. Harel et al. [7] proposed a sugar-beet pectin demethylation method using ammonia that yielded gels with enough mechanical strength and insolubility, suitable for biosorption applications.

After biosorption, the elution of metals could be interesting for the reutilization of exhausted biomass and the recovery of the adsorbed metals. Desorption can be carried out by proton exchange using acids, by exchange with other ions (for example $CaCl_2$) or by chelating agents (EDTA). An efficient eluant is one that desorbs the metal completely without deteriorating the biomass in case it will be reused.

The aim of this work was to determine the effectiveness of sugar-beet pectin gels for the biosorption and desorption of Cd^{2+}, Pb^{2+} and Cu^{2+} from aqueous solutions. There are few studies in the literature related to metal binding with sugar-beet pectins, and only one with calcium gels for one metal, cadmium [7,9,10]. Studies concerning to desorption and reuse of metal-loaded biosorbents are also very rare and none address the use of pectins or their gels. In the present work, sugar-beet pectins were extracted and demethylated to obtain hydro- and xerogels which were used for the biosorption and desorption of three heavy metals: cadmium, lead and copper. The stability of the gel beads in aqueous solutions was tested and the optimum conditions for the biosorption were determined. The biosorption data were fitted to the pseudo-second order kinetic model, and the Langmuir isotherm model, and the corresponding parameters were obtained. This equilibrium and kinetic information is useful to design a full-scale batch process and to predict biosorbent performance and effectiveness. In order to confirm the demethylation and determine possible metal binding mechanisms after metal biosorption, the pectins and their gels were characterized using infrared and microscopy analysis. Finally, the best desorbent of the metal-loaded xerogels was chosen from three types of inorganic acids (HCl, H_2SO_4 and HNO_3 0.1 M).

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 based on the protocol proposed by Harel et al. [7]. The sugar-beet pulp was washed repeatedly 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 the remaining liquid was treated with a solution of 95% ethanol until a pectin precipitate was formed. This ethanol solution becomes impregnated with alcohol soluble residues and cannot be reused. The pectin was filtered and washed repeatedly with ethanol solution: twice with 70% ethanol, and once with 85% and 95% ethanol successively, with enough volume to cover the pectin precipitate in each step. The remaining solid was dried in a stove at 35 °C and ground in an agate mill. The remaining ethanol solution from the last wash (95%) can be mixed and reused with the ethanol of the initial precipitation step after extraction.

The acid-extracted sugar-beet pectin had a high methylation degree and was not suitable for calcium gelation, therefore the pectin had to be demethylated. The demethylation method was adapted from the methods proposed by Harel et al. [7] and Le Cerf et al. [11]. A solution of 2% pectin in deionized water was stirred for at least 2 h and, as described for the extraction process, precipitated with 95% ethanol and filtered with cheesecloth. The pectin was cooled to 4 °C and a solution of ammonia 1 M at the same temperature was added until a 2% pectin solution was obtained. This solution was stirred until homogenized and kept 12 h without stirring at 4 °C. As described earlier, it was precipitated with a 70% ethanol solution, filtered and washed again twice with the ethanol solution. After filtering a third time it was left 6 h stirring in the 70% ethanol solution. For the last washes it was filtered and resuspended in a 85% and 95% ethanol solution successively. The remaining solid was dried in a stove at 35 °C and ground with an agate mortar.

The demethylation procedure was effective in increasing the calcium sensitivity of the pectins and the preparation of calcium pectate beads. Solutions of different concentrations of pectin (1.5%, 2%, 3.5% and 5%) were dropped into different cooled 1 M $CaCl_2$ solutions (0.2, 0.6 and 1 M) to determine the influence of pectin and calcium concentrations on the gelation process. Visual and tactile ("finger test", according to [8]) evaluation determined that the optimum gelation conditions were 1.5% pectin dropped on a 4 °C 1 M $CaCl_2$ solution. The viscous solution was pressed through a syringe (internal diameter of 0.5 mm) to ensure good reproducibility. The beads were kept at 4 °C at least 24 h in the same solution. Excess $CaCl_2$ was rinsed with distilled water. The diameter of the hydrogel beads formed was 3 ± 0.2 mm. The beads were air dried at room temperature (23 ± 1 °C) to obtain the xerogel beads, that measured approximately 1.4 ± 0.2 mm of diameter.