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Biosorption of Zn(II) from industrial effluents using sugar beet pulp and *F. vesiculosus*: From laboratory tests to a pilot approach

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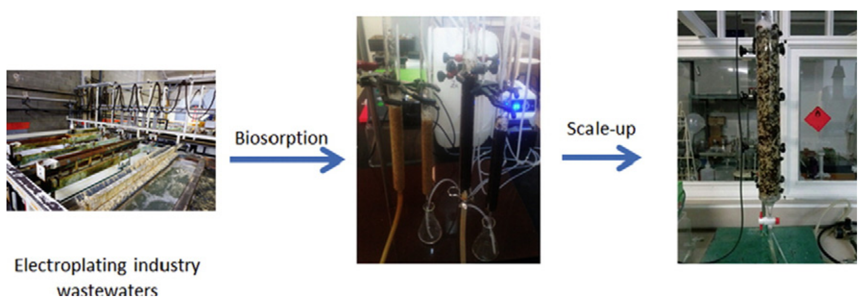
HIGHLIGHTS

- Industrial wastewaters can be treated with F. vesiculosus and sugar beet pulp.
- F. vesiculosus showed higher sorption capacity than sugar beet pulp.
- Wastewaters can be treated in column and serial columns increased the service life.
- The scaling-up allowed the decontamination of higher volumes of dissolution.
- The mixture of biomasses improved the performance of the columns reducing costs.

GRAPHICAL ABSTRACT



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ABSTRACT

The aim of this work was to demonstrate the feasibility of the application of biosorption in the treatment of metal polluted wastewaters through the development of several pilot plants to be implemented by the industry. The use as biosorbents of both the brown seaweed *Fucus vesiculosus* and a sugar beet pulp was investigated to remove heavy metal ions from a wastewater generated in an electroplating industry: Industrial Goñabe (Valladolid, Spain). Batch experiments were performed to study the effects of pH, contact time and initial metal concentration on metal biosorption. It was observed that the adsorption capacity of the biosorbents strongly depended on the pH, increasing as the pH rises from 2 to 5. The adsorption kinetic was studied using three models: pseudo first order, pseudo second order and Elovich models. The experimental data were fitted to Langmuir and Freundlich isotherm models and the brown alga *F. vesiculosus* showed higher metal uptake than the sugar beet pulp. The biomasses were also used for zinc removal in fixed-bed columns. The performance of the system was evaluated in different experimental conditions. The mixture of the two biomasses, the use of serial columns and the inverse flow can be interesting attempts to improve the biosorption process for large-scale applications.

1. Introduction

Heavy metals are very polluting elements that can be accumulated and concentrated in living tissues along the food chain (Mohammed et al., 2011; Tchounwou et al., 2012). In consequence, the treatment of effluents charged with these contaminants is attracting growing interest because of environmental and sanitary problems, and increasingly restrictive legislations (Hosono et al., 2010; Kostarelos et al., 2015; Tóth et al., 2016). The recovery of these metals can also be economically interesting because of its increasingly higher prices (Barakat, 2011). Such effluents pose serious problems for the industry due to the high cost of metal decontamination using conventional technologies. The conventional process of heavy metal removal from industrial wastewater involves chemical precipitation of metals usually by lime followed by settling of the metal precipitates in a pond and/or a clarifier (Charerntanyarak, 1999). The main drawbacks of the conventional treatment include the low efficiency at low concentration of heavy

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metals and the expensive handling and safe disposal of toxic sludges. Apart from physical and chemical methods of treatment, such as filtration and chemical precipitation, electrochemical treatments, reverse osmosis, ion exchange, adsorption and evaporation, biological methods have been in place (Zhao et al., 2016). Biosorption is a cost effective alternative that can be appropriate for treating effluents with low metal concentrations and can also be used to remove other contaminants such as dyes and organic compounds (Chojnacka, 2010; Michalak et al., 2013). It is a property of certain types of organic matter or biomass (biosorbents) to passively bind metals on chemically active sites or functional groups. The type of biomass used determines the metal uptake and the selectivity of the recovery process (Veglio and Beolchini, 1997). Most biosorption studies have been carried out on microbial systems, chiefly bacteria (More et al., 2014), microalgae (Suresh Kumar et al., 2015) and fungi (Gola et al., 2016), and with toxic metals and radionuclides. However, the use of dead biomass makes the process nutrient-independent, faster and increases the metal uptake (Mata et al., 2009; Mehta and Gaur, 2005).

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 (Hegazi, 2013; Nguyen et al., 2013).

This work reports the biosorption of heavy metals (especially zinc) from electroplating industry wastewaters using sugar beet pulp and *Fucus vesiculosus* as biosorbents. Sugar beet (*Beta vulgaris*) pectins can be obtained from sugar beet pulp, a residue of the sugar processing industry. Sugar beet pulp is sold as animal feed at very low prices and it is readily available for revalorization (Kelly, 1983; Mata et al., 2009). Pectins are polysaccharides of the middle lamella and primary cell wall in which they are crosslinked with cellulose and hemicellulose fibers (Kühnel et al., 2011). 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 (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 (Mata et al., 2009).

Fucus vesiculosus has been described as an effective biosorbent of heavy metals (He and Chen, 2014; Mata et al., 2008). Alginate, a component of the outer cell wall of brown algae, is responsible for the high metal uptakes of this biomass when compared to other algae, bacteria and fungi. Alginate is a linear unbranched polysaccharide of alternating blocks of D-mannuronic and L-guluronic acids. They are rich in carboxyl groups, the main functional groups involved in heavy metal biosorption (Bayramoğlu and Yakup Arıca, 2009; Bertagnolli et al., 2014).

In spite of the great progress made over the last decade, the development of biosorption is still mainly at the stage of laboratory studies (Park et al., 2010). Little effort has been made on heavy metal treatment from industrial effluents using agricultural and natural materials in continuous systems. Most studies on continuous biosorption systems have limited industrial application because industrial effluents contain several metal ions and other contaminants (Acheampong and Lens, 2014; Singh et al., 2012). In addition, the use of sorbents for multiple sorption and desorption applications process sustainability leads to a substantial reduction in the raw materials requirement, operational cost and waste materials production (Lata et al., 2015; Mata et al., 2010).

This study is focused on the biosorption of zinc from aqueous effluents by sugar beet pulp and *F. vesiculosus*. Several aspects related with the adsorption were investigated to clarify and compare the zinc adsorption behavior of the biomasses: adsorbent characterization (SEM and FTIR), pH of the solution, adsorption isotherms and biosorption kinetics. In addition, continuous experiments were evaluated by operating columns under different conditions: real and synthetic solutions, desorption (HCl, HNO_3, H_2SO_4, EDTA, acetic acid), scale-up, direct and reverse feed flow and composition of the fixed bed. The experimental data were used to determine the optimum experimental conditions that yielded the highest metal uptakes in order to develop the pilot plants design.

2. Materials and methods

2.1. Biomass

The brown alga *Fucus vesiculosus* was collected in the northern Atlantic coast of Spain. The sugar beet pulp was provided by Azucarera, a company of the ABSugar Group, from its plant in Toro (Zamora, Spain). The pulp was collected directly from the final drying line to ensure freshness and ease of use for the experimentation with respect to the pelletized form. The biomasses were washed, dried in an oven at 60 °C, ground with a mill and sieved through $1.5 < x < 0.5$ mm mesh size.

2.2. Batch experiments

The biosorption experiments were performed with monometallic solutions prepared from stock solutions of 1000 mg/L using chemical reagents of analytical grade: chlorides as in Goñabe wastewaters ($ZnCl_2$ and $CrCl_3 \cdot 6H_2O$). The initial pH of solutions was adjusted with diluted HCl and with NaOH.

Biomasses were placed in contact with the metal solutions in glass Erlenmeyers stirred at room temperature (23 ± 1 °C). Liquid samples were removed at different times (0, 15, 30, 60 and 120 min) and metal concentration was measured periodically. Kinetic studies were performed at pH 5 adding 1 g/L of sorbent to continuously stirred glass Erlenmeyers containing 100 mL of 100 mg/L zinc ions solutions. Adsorption isotherms were also performed at pH and at constant temperature by varying the initial zinc ion concentration from 10 to 600 mg/L.

Sorption isotherms in binary mixtures (Zn^{2+}–Cr^{3+}) at constant pH (being the optimal pH value 5) were determined using the subsequent addition method to multicomponent systems (Pérez-Marín et al., 2008). The different parameters that quantify the process were obtained from the experimental equilibrium data using Matlab 5.1 software. The experiments were carried out in duplicate and the average values were used for data treatment.

2.3. Continuous biosorption tests

Biosorption tests were performed at room temperature in small glass columns (2.5 cm inner diameter and 40 cm length) packed with sugar beet pulp or *Fucus vesiculosus* biomass. The experiments were carried out with both synthetic solutions containing 500 mg/L Zn^{2+} as $ZnCl_2$ and real effluents from Industrial Goñabe (Valladolid, Spain). The initial pH value of the metal solution (5.0) was adjusted with dilute HCl and NaOH. That pH gave the maximum metal uptakes in previous batch studies with these biomasses, besides it is below the precipitation pH at the metal concentration used. The metal solutions were fed from the top of the columns in the drop-fed system using a peristaltic pump (MasterFlex L/S). A series of two consecutive biosorption columns, where the outlet solution of the former column is the inlet solution of the next column, allows the substitution of the saturated portions of the biosorbent in the initial columns without interrupting the effluent treatment. 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.