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Cadmium biosorption by alginate extraction waste and process overview in Life Cycle Assessment context

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ABSTRACT

This work evaluated the cadmium biosorption capacity by the alginate extraction residue from brown seaweed *Sargassum filipendula*, an industry waste which is often discharged into the sea. The biosorption kinetics and equilibrium were investigated, with further analysis of the process thermodynamics. The Mass Transfer in External Film model best described the kinetic data and the rate controlling step is the diffusion through the boundary layer. The kinetic constant values of the model were 0.129, 0.064 and 0.066 1/min for initial concentrations of 1.0, 1.5 and 2.0 mmoL/L, respectively. The isotherms were obtained at four temperatures (293, 303, 313 and 323 K) and were analyzed by Langmuir, Freundlich and Dubinin-Radushkevich models. The system was better described by Freundlich model, and the Dubinin-Radushkevich model suggested that the cadmium uptake is of physical nature. The maximum biosorption capacity obtained at 293 and 303 K were 0.394 and 0.429 mmoL/g, respectively. The thermodynamic parameters indicated that the biosorption of cadmium is spontaneous and exothermic. The simplified LCA showed that the use of dealginated residue would lead to lower environmental impacts for Acidification, Climate Change, Eutrophication, Human Toxicity and Photochemical Oxidation.

1. Introduction

The recent industrial growth has been causing a great impact on ecosystems and on quality of life in cities. Industrial effluents may contain toxic metals, which are hazardous pollutants. They are not easily eliminated from organisms and present potential for biomagnification and bioaccumulation (Barwick and Maher, 2003). Cadmium is a toxic metal largely employed in several processes, including electroplating and pigment production. In human organisms, the presence of cadmium may lead to osteoporosis and damages in kidneys (Åkesson, 2011).

Among the methods for toxic metal removal from effluents, there are chemical precipitation, ion exchange, membrane separation and adsorption (El-Bayaa et al., 2009). Some conventional treatments are expensive and not effective in all range of metal concentration, especially in low concentrations. Membrane separation, such as reverse osmosis or nanofiltration, may require high pressure leading to a high energy cost (Yang et al., 2014). Chemical precipitation may require a large amount of chemicals to reduce the metal concentration to an acceptable value, resulting in extra cost for sludge disposal and may present difficulties to achieve low concentrations defined by stringent regulations (Kurniawan et al., 2006). In this aspect, biosorption has been increasingly studied for toxic metal removal from aqueous solutions. Alternative and economic materials investigated for cadmium biosorption include agricultural (Basu et al., 2017) wastes, fungal (Ma et al., 2015) and algal (Cardoso et al., 2017b; Fagundes-Klen et al., 2007) biomass.

In biosorption processes, toxic metal ions are passively bound to inactive biomass in aqueous solutions (Davis et al., 2003). Several mechanisms take part in metal binding, such as ion exchange, chelation and physisorption (Volesky and Holan, 1995). For biosorption on seaweeds, ion exchange is reported to be the most relevant mechanism in metal sorption (Davis et al., 2003).

Brown seaweeds are efficient on toxic metal sorption. Furthermore, the biopolymer alginate, present in cell walls of brown seaweeds, is a main responsible for metal binding (Davis et al., 2003). Functional groups of alginate are involved in ion exchange reactions with metal ions, resulting in the uptake of metals from

Abbreviations: D-R, Dubunin-Radushkevich; MTEF, mass transfer in external film; ARE, average relative error; LCA, life cycle assessment; LCIA, life cycle impact assessment; FU, functional unit; AC, activated carbon; AEW, alginate extraction waste.

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aqueous phase. *Sargassum filipendula* is a brown algae largely studied: cadmium and zinc in binary system were investigated by Fagundes-Klen et al. (2007); Kleinübing et al. (2013) evaluated the biosorption of lead, copper, cadmium and zinc ions on raw seaweed and on the extracted alginate; Volesky et al. (2003) studied the uptake of copper in a column. On the other hand, brown algae are also raw material for alginate production through extraction, which has applications in food and textile industries (Bertagnolli et al., 2014). In alginate extraction process, it is generated a fibrous residue, which has limited use. This leftover pulp is mainly thrown back into the sea (Kumar and Sahoo, 2017). However, it still contains components of the raw algae and would be employed as a biosorbent of toxic metals (Cardoso et al., 2017a; Costa et al., 2016).

In industry, the use of biosorption is being studied and tested. Michalak et al. (2013) cited two examples of companies offering biosorbents based on algae: Bio-Recovery System (Las Cruces, USA) and B.V. SORBEX (Montreal, Canada). On the other hand, some factors still limit a wider industrial application, such as elevated economic value (Macek and Mackova, 2011). In AEW case, there is not a relevant economic value since it is a residue. However, a limiting factor would be the AEW regeneration for biosorption-desorption cycles in fixed-bed columns for industrial treatment, which is also being studied (Moino et al., 2017).

Life Cycle Assessment (LCA) is a method widely used to evaluate the environmental performance of a product or service (European Comission - Joint Research Centre - Institute for Environment and Sustainability, 2010). Many low cost and alternative materials are investigated for adsorption; however little studies have been conducted to assess the environmental performance of these materials (Dodbiba et al., 2009; Yami et al., 2015).

Therefore, this work aims to investigate the use of the AEW (alginate extraction waste) from the brown seaweed *Sargassum filipendula* as biosorbent for cadmium removal, providing a comprehensive analysis of the kinetics and equilibrium aspects of the cadmium uptake. In addition, the benefits for environment related to the reuse of the AEW are evidenced by the comparison with a commercial adsorbent (AC, activated carbon), in lab scale using the LCA method. The innovative character of this study is the extensive and in-depth investigation of the application of the AEW in toxic metal removal, adding value to the seaweed chain.

2. Material and methods

2.1. Biosorbent material

The brown seaweed *Sargassum filipendula* was collected at São Sebastião ("Cigarras" beach), State of São Paulo, in November of 2015. Costa et al. (2016) characterized the raw seaweed and the residue after alginate extraction.

The raw seaweed presented small diatoms in its structure, similarly as the residue after alginate extraction. In chemical composition, the content of Si decreased due to diatoms release and the content of sodium increased in extraction process. FTIR spectra indicated that the residue maintains functional groups such as carboxylic acids, sulfonate and amino groups, even after alginate extraction, which suggests that AEW has potential to be used as a biosorbent material (Costa et al., 2016).

2.2. Preparation of biosorbent

The seaweed was washed to remove sand and dried in an oven at 60 °C for 24 h. The algae was milled and sieved into fractions smaller than 1 mm. The alginate was then extracted following the method described by Mchugh (1987).

Fifteen g of the raw algae were placed in contact with 500 mL of an aqueous solution of formaldehyde (0.4% w/w) for 30 min. The algae were rinsed and added to 500 mL of hydrochloric acid solution (0.1 moL/L) for 2 h. Formaldehyde and hydrochloric solutions were applied to clarify the material and remove phenolic compounds. The alginate extraction was performed with 350 mL of a sodium carbonate solution (2% w/v) for 5 h at 60 °C. The mixture was filtered to separate the fibrous residue and the liquid phase with the solubilized alginate. In the presence of sodium carbonate, alginate is converted to a soluble form (Davis et al., 2003) and can be separated from the solid phase.

The AEW was exhaustively washed with deionized water. Ethanol (1:1 v/v) was used for the alginate precipitation. The residue and the precipitated alginate were dried at 60 °C for 24 h. Then, the residue was milled and sieved into fractions with an average diameter of 0.737 mm. The yield of residue and alginate were calculated by Equations (1) and (2).

$$\%Yield\ (Residue) = \frac{final\ dry\ matter\ of\ residue}{seaweed\ dry\ matter\ before\ extraction} \cdot 100 \quad (1)$$

$$\%Yield\ (Alginate) = \frac{final\ dry\ matter\ of\ alginate}{seaweed\ dry\ matter\ before\ extraction} \cdot 100 \quad (2)$$

2.3. Cadmium solutions

The Cd(II) solutions were prepared by dissolving cadmium nitrate ($Cd(NO_3)_2.4H_2O$), analytical grade (Vetec, Brazil), in deionized water. The pH was adjusted to the required value with nitric acid (0.1 moL/L) solution.

Cadmium concentration was determined by atomic absorption spectrophotometer (AAS) AA-7000, Shimadzu (Japan).

2.4. Biosorption studies

Kinetic (Nishikawa et al., 2016) and equilibrium studies in batch mode were carried out to analyze the sorption of cadmium on the AEW. The biosorbent dose was fixed at 2 g/L and the pH was maintained at 3.5.

In the kinetic study, 500 mL of Cd(II) solutions with three different initial concentrations (1.0, 1.5 and 2.0 mmoL/L) were stirred with 1 g of biosorbent at room temperature (20 °C). At predetermined time intervals, solution samples were taken and the residual cadmium concentrations were analyzed by atomic absorption. The Table S4 (Supplementary Material) presents the average results of three measurements and the deviations.

Biosorption isotherms of Cd(II) were obtained through series of 50 mL solutions with different initial concentrations (0.5–18 mmoL/L) in capped Erlenmeyer flasks of 100 mL. The bioadsorbent (0.1 g) was added to each flask and the system was maintained under constant agitation (150 rpm) and temperature (293, 303, 313 and 323 K). The contact time was determined in the kinetic study.

The amount q of metal adsorbed (mmol/g) and the removal percentage (%Rem) were calculated from the Equations (3) and (4):

$$q = (C_0 - C_e)\ V/m \quad (3)$$

$$\%Rem = C_0 - C_e/C_0 \cdot 100 \quad (4)$$

where: V is the volume of solution (L), m is the mass of dry