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Zinc and cadmium biosorption by untreated and calcium-treated *Macrocystis pyrifera* in a batch system

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ABSTRACT

Zinc and cadmium can be efficiently removed from solutions using the brown algae, *Macrocystis pyrifera*. Treatment with $CaCl_2$ allowed stabilization of the biosorbent. The maximum biosorption capacities in mono-component systems were 0.91 mmol g^{-1} and 0.89 mmol g^{-1} and the Langmuir affinity coefficients were 1.76 L $mmol^{-1}$ and 1.25 L $mmol^{-1}$ for Zn(II) and Cd(II), respectively. In two-component systems, Zn(II) and Cd(II) adsorption capacities were reduced by 50% and 40%, respectively and the biosorbent showed a preference for Cd(II) over Zn(II). HNO_3 (0.1 M) and EDTA (0.1 M) achieved 90–100% desorption of both ions from the loaded biomass. While HNO_3 preserved the biomass structure, EDTA destroyed it completely. Fourier transform infrared spectra identified the contribution of carboxylic, amine and sulfonate groups on Zn(II) and Cd(II) biosorption. These results showed that biosorption using *M. pyrifera*-treated biomass could be an affordable and simple process for cadmium and zinc removal from wastewaters.

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1. Introduction

Cadmium is one of the most toxic metals (Luna et al., 2010). The major sources of cadmium released into the environment are water streams from electroplating, smelting, alloy manufacturing, pigments, plastic, battery, mining, and refining process. Cadmium tends to accumulate in living organisms causing significant threats to both, the environment and public health (Xiao et al., 2010). Zinc is an essential element for humans at low concentrations since it stimulates the activity of more than a hundred enzymes and plays an important role in the immune system. However, at high concentration it becomes toxic (Boschi et al., 2011). This metal is extensively used for galvanization and manufacturing of brass and other alloys, and in batteries and pigments (Luna et al., 2010).

The US EPA requires zinc and cadmium in drinking water not to exceed, 5 and 0.005 mg L^{-1}, respectively. Techniques used to remove/reduce the metal contents of wastewater include chemical precipitation, adsorption (on activated carbon), ion exchange, evaporation and membrane processes (Volesky, 2003). Adsorption by activated carbon is the most efficient process since it removes more than 99% of some metal ions, but the operative costs are prohibitive when treating large volumes or dilute effluents. In addition this adsorbent cannot be readily regenerated and recycled (Farooq et al., 2010). These methods mostly treat metal ions as a waste to be eliminated (landfill) with limited possibilities to recycle or valorize the materials. Some of the methods (e.g., precipitation and coagulation) produce concentrated and toxic wastes which require controlled storage and landfill disposal.

Hence, there is a need to search for an optimal technology for metal recovery. In recent years, biosorption has emerged as a cost-effective and efficient alternative for removal of heavy metals from waste waters. Microorganisms such as algae, bacteria, yeast, fungi, but also agricultural by-products (including plants leaves and root tissues) can be used as biosorbents for detoxification and recovery of toxic or valuable metals form industrial discharges. Algae are among the most promising biosorbents. Skowronski and Przytocka-Jusiak (1986) reported the sorption of cadmium onto the green micro-algae *Sitchococcus bacilliaris*. The algae most frequently studied as biosorbents are *Ascophyllum nodosum* (Carvalho et al., 1995), *Fucus vesiculosus* (Mata et al., 2008), *Laminaria japonica* (Febrianto et al., 2009), and various species of the genus *Sargassum* (Fagundes-Klen et al., 2007; Luna et al., 2010). *Macrocystis pyrifera* is a brown alga (Phaeophyta) that grows in water along the south coast of Argentina. *M. pyrifera* is frequently deposited on the beach of Bahía de Camarones causing unpleasant odors and a negative impact on local tourism and can be considered an easily available natural waste (Plaza et al., 2011, 2012). There are very few reports on the use of *M. pyrifera* as biosorbent for heavy metal removal. Seki and Suzuki employed *M. pyrifera* for the adsorption of cadmium and lead (Seki and Suzuki, 1998) and Plaza et al. (2011, 2012) used this algae for the removal of Hg(II) and Cr(III) from aqueous solutions. The presence of alginate in its cell

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