Brown macro-algae as natural cation exchangers for the treatment of zinc containing wastewaters generated in the galvanizing process

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A B S T R A C T

In this study, brown macro-algae harvested from the north coast of Portugal, *Laminaria hyperborea*, *Fucus spiralis*, *Pelvetia caniculata* and *Ascophyllum nodosum*, were used as natural cation exchangers for the treatment of zinc-containing rinse waters generated in the galvanizing process. The zinc wastewater is characterized by a high conductivity (1.5 mS/cm), a low organic content and a zinc concentration of 10 mg/L, being approximately 80% and 20% in the form of Zn^{2+} and $ZnSO_{4(aq)}$, respectively.

Although the ion-exchange capacity of the four macro-algae is similar (2.2—2.4 mEq/g), mainly associated with the presence of weak acidic carboxylic and strong acidic sulfonic groups, *L. hyperborea* showed a higher selectivity for zinc ions. The uptake capacity for zinc ions is highly affected by the galvanic wastewater matrix, when compared with the performance using a pure zinc solution. Zinc uptake equilibrium, on all the natural cation exchangers, was well described by a linear relationship. Cation exchange kinetic was adequately represented by a mass transfer model, considering a linear driving force model for intraparticle diffusion. Na-loaded alga showed a higher affinity for zinc ions when compared with Ca-loaded alga and raw alga. HCl, HNO_3, H_2SO_4 and $CaCl_2$ eluents were tested for zinc displacement from exhausted algae. HNO_3 reached an elution efficiency of 100% in less time than the other eluents tested. After the acid elution, the resin was converted to Na or Ca form (Na- or Ca-H-loaded biomass), using NaCl and $CaCl_2$ solutions. Although the regenerated alga in the form of sodium showed a higher affinity for zinc ions, its physical deterioration after Na loading may affect its application in a full-scale treatment.

1. Introduction

For over a century, zinc has been used to enhance the longevity and performance of steel or iron, in a process known as galvanization (NPi, 1999). This technique generates a large volume of wastewater from rinse waters and exhausted acid pickling baths loaded with heavy metals such as zinc, iron, copper and hexavalent chromium, which are harmful to health and the environment (Marañón et al., 2005). Treatment technologies for the removal of heavy metals from galvanic wastewaters include chemical precipitation, membrane filtration, electrochemical processes, ion exchange and adsorption/biosorption (Naja and Volesky, 2009). The most common treatment applied to galvanic wastewaters is chemical precipitation, which is a simple technique, not metal selective and inexpensive capital cost, but at the end, a large volume of hazardous sludge is generated, causing economic and environmental problems. The membrane filtration has as advantages the low quantity of chemical consumption, small space for operation and small volume of solid waste produced but, on the other hand, the initial investment and running costs makes the process uneconomical. Electrochemical process is a technique where no chemical reagents are required, it has low operational costs and pure metals can be obtained, nevertheless, due to H_2 and O_2 formation during the process, current efficiency is low. Ion exchange allows to achieve treated water with extreme good quality, recovering the metals from the galvanizing baths and rinses wastewaters, as also the wastewater reuse in the galvanization process, minimizing chemicals and water consumption. However, ion exchange resins are expensive. The adsorption process offers flexibility in design and operation, present high removal capacity, fast kinetics and availability of different adsorbents as well as cost effectiveness

but, the performance depends upon the type of adsorbent (O'Connell et al., 2008). Among them, biosorption has been proposed as an cost effective and eco-friendly technology for the removal of several metals from wastewaters (Bulgariu and Bulgariu, 2016). Several metal-binding mechanisms have been proposed to be active in biosorption such as physisorption, chemisorption, ion exchange and microprecipitation (Robalds et al., 2016). Ion exchange is the dominant binding mechanism in brown marine macro-algae and seaweeds have been established as natural cation exchangers for the sequestration of positively charged metal ions, such as lead, zinc, copper, cadmium, cobalt and others. This is mainly associated with the presence of weak acidic carboxylic and strong acidic sulfonic functional groups on their surface, which can act as binding sites for metal cations (Davis et al., 2003). Raw macro-algae are in the form of K^+, Na^+, Ca^{2+} and Mg^{2+}, which salts are present in seawater at high concentration. The cation exchange takes place by replacement of those alkaline and alkaline earth metals by other metals, such as transition metals. Beyond that, these natural resins can be used not only in K^+, Na^+, Ca^{2+} and Mg^{2+} forms, as also in the protonated form, by performing an acid preliminary pre-treatment. Additionally, metal-loaded algae can be regenerated and the small volume of eluent with a high metal concentration can be reused in the galvanic process or metals can be extracted by routine commercial methods, increasing thus, the cost effectiveness of the process. Furthermore, the regenerated macro-algae can be reused in multiple saturation/elution/regeneration cycles (Naja and Volesky, 2009; Volesky, 2003).

Several papers have been published regarding the use of macro-algae as natural cation exchangers for heavy metals removal from pure solutions under laboratory conditions. Liu et al. (2009) studied the biosorption of Cd^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} ions from aqueous solutions by pre-treated *Laminaria japonica*. The results showed that the pretreatment with Epichlorohydrin crosslinking was the most efficient, presenting maximum uptake capacities of 1.85, 1.78, 1.13 and 1.42 mmol/g, respectively for Cd^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} at initial pH between 4.8 and 6.0. Carro et al. (2015) used Ca-pretreated *Sargassum muticum* for the removal of Hg(II) and Cd(II) from synthetic solutions, achieving maximum uptake capacities of 0.80 and 1.49 mmol/g, respectively, at 25 °C and natural pH.

However, the composition of real industrial effluents is much more complex than pure metal solutions, frequently presenting large amounts of light metals ions and other contaminants. This can compromise the biosorption performance for transition metals removal, due to competition between light metal ions (as also other inorganic and organic contaminants) and the metals of interest (Vijayaraghavan and Balasubramanian, 2015). The quite scarce information about the treatment of real effluents using biosorption technology, has up to now been one of the main reasons for the absence of industrial applications in this field. This paper attempts to serve as a step forward in this subject.

Therefore, the main goal of this work is the use of four brown macro-algae, *Laminaria hyperborea*, *Fucus spiralis*, *Pelvetia caniculata* and *Ascophyllum nodosum*, abundant in the north coast of Portugal, as natural cation exchangers for the treatment of zinc containing wastewater generated in the galvanizing process. Equilibrium and kinetic ion-exchange loading assays were performed in batch system in order to select the macro-algae with the highest affinity for zinc ions present in the galvanic wastewater. Elution studies were also performed using different eluents, such as H_2SO_4, HNO_3 and HCl (1.0 < pH < 2.0) and $CaCl_2·2H_2O$ (0.1–0.5 M). The regeneration step was also evaluated using calcium or sodium concentrated salt solutions (0.5 M $CaCl_2$ ·2H_2O and 0.5 M NaCl).

This paper is organized in the following way: Section 2 details the methodology used to concretize the study including the analytical methods and procedures applied for saturation/elution/regeneration ion-exchange experiments in batch mode; galvanization process description and wastewater origin/pre-treatment; algae and wastewater characterization; Section 3 reports and discuss the saturation/elution/regeneration ion-exchange results, including the equilibrium and mass transfer models developed; Section 4 provides the main conclusions and suggestions for future work.

2. Experimental methods

2.1. Biomass preparation

The seaweeds − *L. hyperborea*, *F. spiralis*, *P. caniculata* and *A. nodosum* − were collected at Viana do Castelo ("Praia Norte" beach), northern coast of Portugal, during May and September of 2013. The seaweeds were washed with tap water and deionized (D.I.) water to remove sand and excess salts. Then the seaweeds were sundried and further dried in an oven at 45 °C during 24 h. The dried seaweeds were then crushed in an electrical mill with a sieve size of 8.0 mm (*Retsch*, SM 2000); this way the thin plate particles length was lower than 1 cm.

2.1.1. Biomass modification

The raw algae was modified to sodium and calcium forms by contacting the particles with 0.5 M chloride solutions (NaCl and $CaCl_2.2H_2O$, respectively) in two 12 h-cycles, under slow stirring (biomass concentration of 10 g/L) (Girardi et al., 2014). After each cycle, the old solution was replaced by a fresh one. Afterwards, the Na- and Ca-loaded algae were rinsed with D.I. water to remove the excess of ions on the surface of the biomass until achieve a low conductivity solution. At the end, the algae were dried at 45 °C for 24 h and stored until use.

For regeneration studies, 10 g/L of alga was protonated by soaking into 0.2 M HNO_3, under slow stirring, during 2 consecutive cycles of 3 h. After each cycle, the old solution was replaced by a fresh one. The protonated alga was then converted to Na- and Ca-H-forms by soaking them into 0.5 M NaCl and $CaCl_2·2H_2O$ solutions, respectively, for 2 cycles of 12 h each, under slow stirring. The solution pH was controlled at 4.0–5.0 by using 1.0 M NaOH. Afterwards, the Na- and Ca-H-form algae were rinsed with D.I. water until achieve a low conductivity solution. The Na- and Ca-H-form algae were dried at 45 °C for 24 h and stored until use.

2.1.2. Biomass characterization/digestion

The amount of alkali (Na^+, K^+) and alkaline earth metals (Ca^{2+}, Mg^{2+}) on the algae surface was determined by digesting ca. 0.5 g of algae in VELP Scientifica DK6 heating digester at 150 °C during 2 h after the addition of 5.0 mL of ultra-pure water, 4.0 mL HNO_3 65% (Sigma−Aldrich) and 12 mL HCl 33.8% (JMGS) (Table 1). After cooling, the digested sample was filtered under vacuum through 0.45 μm cellulose acetate filter (Specanalitica) and the volume was completed to 50 mL with ultra-pure water. The metal concentrations in the digests were determined by flame atomic absorption spectrometry (AAS) as described forward.

The apparent density of the algae was determined by mercury intrusion porosimetry using a Quantachrome PoreMaster®. Real density was determined by helium pycnometry. The algae were previously grinded to powder and dried at 45 °C overnight to remove humidity.

The identification of the functional groups on the surface of the biomass particles was performed by infrared spectrometry using a Shimadzu FTIR IRAffinity spectrometer. The samples were ground and dried at 45 °C for 24 h and analyzed in the solid form using a diffuse reflectance accessory (Pike Technologies Inc., model TM EasiDiff). Spectra were registered from 4000 to 400 cm^{-1}.