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Removal of Zinc by adsorption on macroalgae as adsorbent from aqueous solution

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Abstract

Discharge of industrial and domestic effluents in environment is responsible for the presence of toxic metals in water, soil and biota. Biosorption, with dead biomass, is a process that allows the passive capture of metal ions by different mechanisms. The objective was to evaluate the use of dry macroalgae in zinc removal from aqueous solution. The effect of alga species, pH, initial adsorbate and adsorbent concentration were evaluated. Results showed that Zn removal efficiency was higher when *Halymenia* sp. (red alga) was used instead *Ulva lactuca* (green alga). This could be related to the different cell wall composition for each algae class. The increase of the adsorbent mass improved the efficiency, and more acidic pHs decreased it. We concluded that algae are an interesting biomass for the removal of zinc.

1. Introduction

Discharges of untreated or inadequately treated wastewater contribute to the release of different types of pollutants into water bodies [1]. Industrial effluents mainly contribute with metal ions to the environment where they are discharged [2,3]. Contamination by heavy metals is a serious environmental problem, because they are potentially toxic, persistent, non-degradable and can bioaccumulate, which facilitates their entry into the food chain and their dispersion [1,4].

Zinc present in the environment has both natural and anthropic sources. It is used in the galvanizing industry, in the manufacture of alloys, batteries and pigments [5]. It is considered an essential element for human at low concentrations, because it is required in many metabolic functions, it is usually presented as an enzymatic cofactor, plays an important role in the immune system and also as a component of the cellular structure; however, in high concentrations it can be toxic [2]. The United States Environmental Protection Agency (US EPA) requires zinc in drinking water not to exceed, 5 mg L^{-1} [5].

There are different methods for zinc and other toxic metals removal from aqueous solutions. We can mention: chemical precipitation, ion exchange, adsorption (on activated carbon and other inorganic materials) and reverse osmosis, among others [6]. These methods consume much energy and chemical reagents, and they are not very effective when applied in diluted solutions [7]. There is a growing interest in developing and evaluating alternative, more environmentally friendly and economical methods for effluents and treatment of aqueous solutions [8]. In this context, adsorption is considered a cost-effective and efficient method for removal of metal ions from industrial effluents or waste waters due to its multiples advantage [9,10].

In particular, biosorption is characterized by the capture of metal ions by living or dead biomass, through physical and chemical mechanisms that occur at the cell surface, and involves the various exposed functional groups of the cell walls [11]. The additional advantage of using dead biomass as biosorbent is that the toxicity of the solution to be treated should not be taken into account. Microorganisms (such as algae, bacteria, yeast, and fungi), plants and even agricultural and industrial wastes can be used as biological materials for the removal and recovery of toxic elements and organic compounds from industrial effluents [12-14]. Special attention has recently been given to the use of macroalgae as an adsorbent, because they have numerous advantages over other materials [15-17]. In addition to being an efficient biosorbent for the elimination of different types of contaminants, algae are a low-cost material, because it is a renewable resource, easy to collect, widely available, in many cases considered waste and when dehydrated, it can be stored for long periods of time without losing its properties [12,18]. Macroalgae are divided into three types: red (Rhodophyta), green (Chlorophyta), and brown algae (Phaeophyta). Differences among these groups are mainly related to the cell wall composition, where adsorption takes place. Mostly research on adsorption with algae involves brown algae [5,19-21] and less extent with green and red algae [22,23]. Cell walls of brown algae are mainly composed of cellulose, alginic acid, and sulphate polysaccharides (fucoidan matrix) [24]. In red algae, in addition to cellulose, it is found sulphated polysaccharides made of galactanes (agar and carragenates) with a known role in biosorption. In cell walls of green algae become relevant a high percentage of proteins bonded to polysaccharides to form glycoproteins. Then, metal biosorption depends on both the structure and composition of the cell wall and the functional groups present (amino, carboxyl, sulphate and hydroxyl) which show different metal affinity [24,25].

The objective of the present work is to evaluate the use of dry algal material as biosorbent, in the removal of zinc from aqueous solutions under different experimental conditions.

2. Material and Methods

2.1. Biological material

Ulva lactuca (green algae) and *Halymenia* sp. (red algae) were collected on the coast of Mar del Plata, Province of Buenos Aires, Argentina (38°00'S 57°33'W) in August 2018. Fresh algae biomass was carefully washed with distilled water in the lab to remove salt, sand and microorganisms. Then, the samples were frozen, lyophilized, and finally ground to obtain fine particles. Finally, the material was stored in plastic bags, in the dark, and at room temperature, until use.

2.2. Reagents and equipment

All chemicals used were of analytical reagent grade and were used without further purification. All solutions and algal suspensions were prepared using Milli-Q water with a resistivity of 18.0 M cm. Stock zinc(II) solution (1000 mg Zn L^{-1}) for the experiments was prepared by dissolving $ZnSO_4 \cdot 7H_2O$.

2.3. Biosorption studies

For the batch experiments, different Zn solutions were prepared from a 1000 mg Zn L^{-1} stock solution. Three initial concentrations were evaluated: 10 mg L^{-1}, 20 mg L^{-1} and 100 mg L^{-1}. The pH was set at different initial values (i.e. 3.0 and 5.7). The most acidic pH value was adjusted using a concentrated nitric acid solution (Biopack). Besides, the effect of the concentration of the adsorbent was also assessed. The experiments were performed using two concentrations of alga biomass (1 g L^{-1} and 5 g L^{-1}).

The experimental model consisted of a batch system under constant agitation (200 rpm) at room temperature. The initial solution volume was 100 mL. Samples were taken and filtered through a 0.45 µm nylon membrane at different time intervals. Control tests were performed in the absence of adsorbent material and in absence of Zn. All experiments were carried out in duplicate.

2.4. Analytical methods

Zn concentration in solution was determined by Atomic Absorption Spectrophotometry (GBC, Model:SensAA). The amount of metal adsorbed (q) was calculated by the following equation:

$$q = \frac{V \cdot (C_i - C_f)}{m} \qquad \text{Equation (1)}$$

where q is the solute uptake (mg g^{-1} or mmol g^{-1}); C_i and C_f are the initial and final concentrations of the solute in the solution (mg L^{-1} or mM), respectively; V is solution volume (L) and m the mass of the biosorbent (g, dry weight).

2.5. Analytical methods

One-way analysis of variance (ANOVA), followed by post hoc Tukey testing if a significant difference was found (IBM SPSS Statistics). A significant level of $p < 0.05$ was accepted for all statistical analysis.

3. Results and discussion

3.1 Biosorption studies

Effect of initial Zn concentration. The study of the variation of the metal uptake as a function of time at different initial Zn concentrations is shown in **Figure 1**. The best results were observed in the experiments carried out with the highest concentrations of Zn (100 mg L^{-1}), both for *Ulva lactuca* and *Halymenia* sp. ($p < 0.05$). Regarding algae species, the maximum amount of metal adsorbed was recorded when red algae were used as biosorbent ($p<0.01$). This result is in agreement with similar experiments of Zn adsorption on different species of red and green algae [22,23]. This could be explained by the characteristics and composition of the cell wall of the different algae classes, which play a fundamental role in the interaction with the metal ions in solution because adsorption is a superficial process. In that sense, red algae are characterized by the presence of a polysaccharide called carrageenan and green algae by the ulvan, with different affinity for metal ions [23,26]. As shown in **Figure 1**, the adsorption proceeded in two steps: a fast uptake, where approximately 70% of zinc elimination occurred in the first 30 min, followed by a slower uptake rate to equilibrium, and the process stops. The equilibrium was reached within 60 min for all experimental conditions.

Effect of the adsorbent concentration. The biomass concentration is an important variable during metal uptake (**Figure 2**). Our results show that the addition of biomass did not increase the amount of Zn adsorbed. Even a significant decrease in the metal ion uptake capacity is observed when the concentration of *Halymeneacea* sp. was increased ($p < 0.05$). Similar results were obtained by other authors. Romera et al. (2007) [25] mention that at a given equilibrium concentration, the biomass takes up more metal ions at lower than at higher cell densities. It has been suggested that electrostatic interactions between cells can be a significant factor in the relationship between biomass concentration and metal uptake. For a given initial metal concentration, the lower the biomass concentration in suspension, the higher will be the metal/ biosorbent ratio and also the metal retained by the adsorbent unit, unless the biomass reaches saturation. High biomass concentrations can exert a shell effect, protecting the active sites from being occupied by metal. The result of this is a lower specific Zn adsorption, that is, a smaller amount of metal uptake per biomass unit [25].

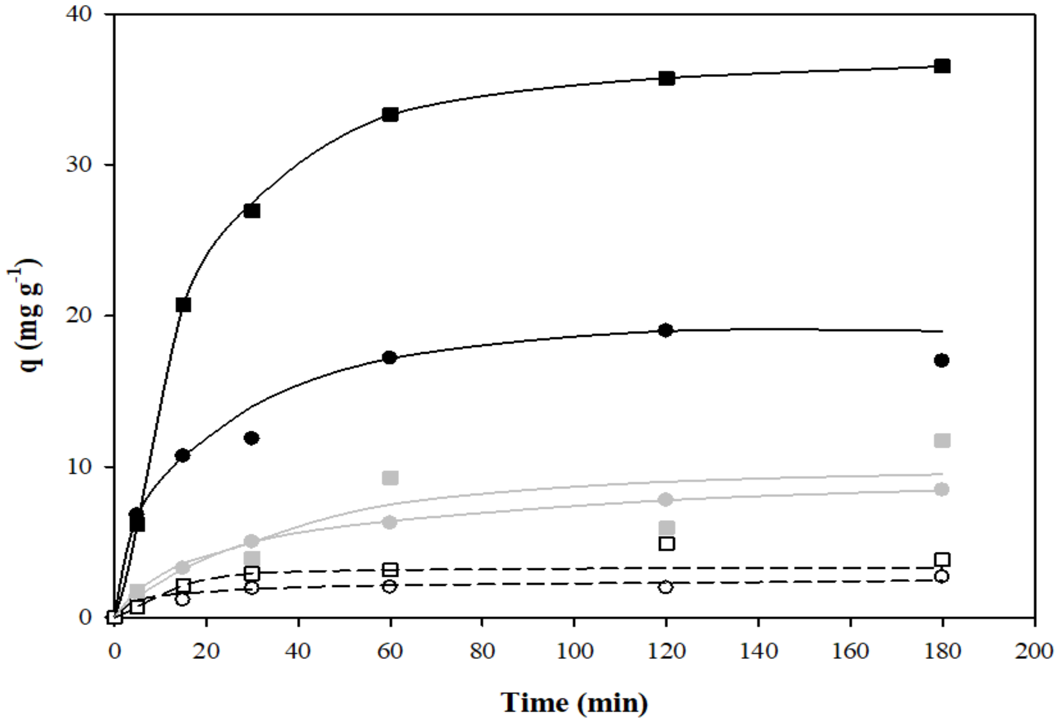

Figure 1: Variation of Zn concentration in solution as a function of time. [Adsorbent] = 1 g L^{-1}; pH = 5.7; ambient temperature; constant shaking. Symbols: ● *U. lactuca*, [Zn]=100 mg L^{-1}; ● *U. lactuca*, [Zn]=20 mg L^{-1}; ○ *U. lactuca*, [Zn]=10 mg L^{-1}; ■ *Halymenia* sp. [Zn]=100 mg L^{-1}; ■ *Halymenia* sp. [Zn]=20 mg L^{-1}; □ *Halymenia* sp. [Zn]=10 mg L^{-1}.

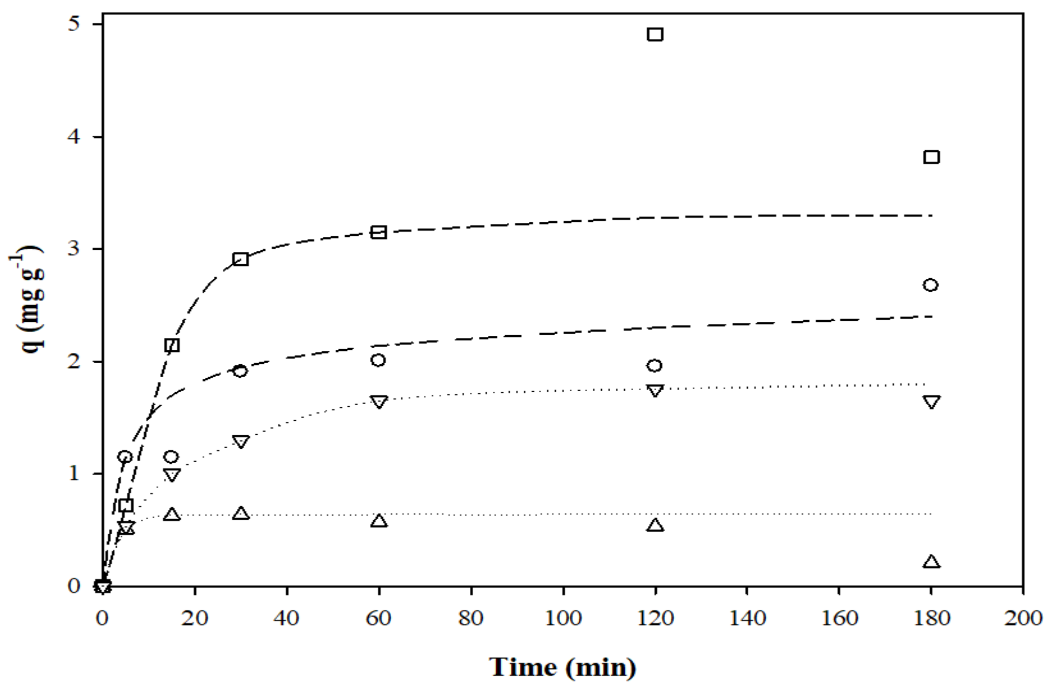

Figure 2: Variation of Zn concentration in solution as a function of time. [Zn]= 10 mg L^{-1}; pH = 5.7; ambient temperature; constant shaking. Symbols: ○ *U. lactuca* 1 g L^{-1}; △ *U. lactuca* 5 g L^{-1}; □ *Halymenia* sp. 1g L^{-1}; ▽ *Halymenia* sp. 5 g L^{-1}

Effect of initial pH. The pH influence on Zn uptake of *U. lactuca* and *Halymenia* sp. is shown in **Figure** 3. No significant differences were observed in the amount of Zn adsorbed in relation to the variation of pH ($p < 0.10$). This coincides with what has been reported in other article which indicate that at pHs below 3.0, there is a reduction in the efficiency of Zn [27]. However, other studies mention an increase in efficiency at pHs above 5 [22,23].

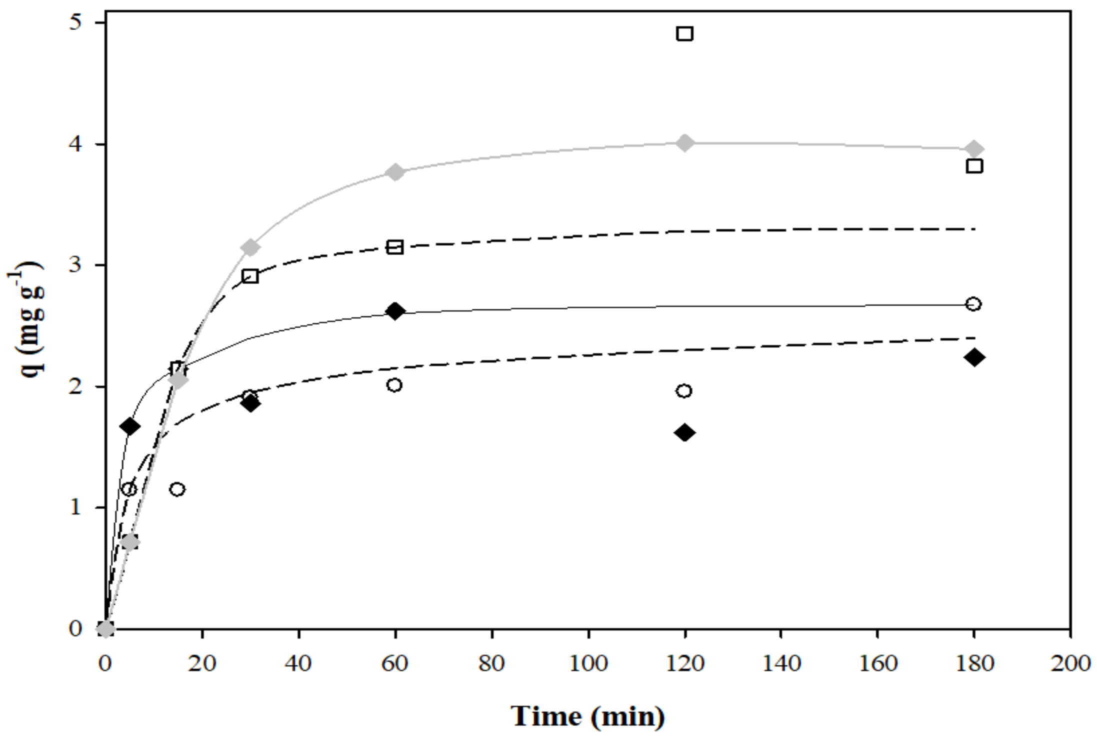

Figure 3: Variation in the concentration of Zn in solution as a function of time [Zn]=10 mg L^{-1}; [Adsorbent] = 1 g L^{-1}. pH = 5.7 and 3.0; ambient temperature; constant shaking. Symbols: ○ *U. lactuca*, pH = 5.7; ◆ *U. lactuca*, pH =3.0; □ *Halymenia* sp. pH = 5.7; ◆ *Halymenia* sp., pH = 3.0.

3.2 Biosorption isotherm models

The Langmuir adsorption isotherm assumes that the adsorption takes place at specific homogeneous surface sites within the sorbent and has found successful application in many adsorption processes of monolayer adsorption. The nonlinear Langmuir model can be expressed by equation (2):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad \text{Equation (2)}$$

where q_e is the amount of sorbate sorbed per unit mass of adsorbent (mg.g^{-1}), k_L is the Langmuir constant related to the sorption capacity (L g^{-1}), C_e is the concentration of sorbate in the solution at equilibrium (mg L^{-1}), q_m is the maximum uptake per unit mass of adsorbent (mg.g^{-1}).

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. It assumes neither homogeneous site energies nor limited levels of adsorption. The nonlinear representation of the Freundlich model is as in equation (3):

$$q_e = K_F C_e^{1/n} \qquad \text{Equation (3)}$$

where K_F (mg.g^{-1}) (L mg^{-1})^n and 1/n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

Fittings to Langmuir and Freundlich adsorption models were made to determine which best describes the process of Zn(II) adsorption in *U. lactuca* and *Halymenia* sp. (**Table 1**). Experimental data exhibited a good fitting with both models. The Langmuir isotherm assumes monolayer adsorption and indicates a reduction of the available interaction places to the extent the metal ion concentration increases [22]. The maximum adsorption capacity (q_{max}) and the affinity coefficient (R_L) were higher in *U. lactuca* than *Halymenia* sp. Freundlich isotherm assumes a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface [22]. Thus, the Freundlich model predicts multi-layer adsorption on the surface of the adsorbent. K_F is the Freundlich constant and reflects the adsorption capacity and 1/n is the degree of heterogeneity. Both parameters were higher for *Halymenia* sp. in concordance with our results.

Table 1: Parameters obtained by plotting experimental data with Langmuir and Freundlich isotherms models for the adsorption of Zn(II) by *U. lactuca* and *Halymenia* sp.

	Langmuir			**Freundlich**		
	q_{max} (mg g^{-1})	K_L	R^2	K_F (L mg^{-1})	1/n	R^2
U. lactuca	126.58	0.04	0.999	3.09	0.63	0.996
Halymenia sp.	91.74	0.02	0.850	14.91	0.87	0.999

Conclusion

Our results show that Zn removal from aqueous solution using dry algae biomass as adsorbent material is a simple and efficient treatment and represents an alternative for metal remediation. In a short time, using *Halymenia* sp. as adsorbent material, it is possible to obtain Zn removal values close to 80%. Besides, it can improve by supporting the biomass on inert materials or activation of biomass using different chemical and physical treatments. It is also interesting to study multi-elemental solutions or real solutions, which allow us to explore the adsorption efficiency in the presence of different metal ions. It shows how much there is still to explore in this field.

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