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A COMPARATIVE STUDY OF Zn(II) IONS BIOSORPTION FROM AQUEOUS SOLUTION ON RED MARINE ALGAE BIOMASS AND ALGINATE

BY

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Abstract. The current trend of specialized research in environmental bioremediation is focused on studies related to the biosorption of metal ions on biological materials. Algae biomass is of great interest due to the significant amount of waste found on our Romanian beaches, which is why several researchers have studied its possibility of being used in environmental remediation processes. Because, marine algae biomass has a modest capacity to retain metal ions from aqueous solutions, the extraction of active compounds from their composition could be a solution to increase biosorptive performance in metal ion removal processes. Alginate is an active compound obtained from marine red algae biomass. In this study, we tested the biosorption performance of red algae sp. *Callithamnion corymbosum* and alginate extracted from them, in retaining Zn(II) ions from aqueous solutions.

Keywords: Alginate; red marine algae; biosorption; Zn(II) ions; aqueous solution.

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1. Introduction

Heavy metal pollution is a major environmental problem, due to its toxicity, persistence and accumulation tendency, high concentrations of heavy metals are found in the environment, becoming an important factor in degrading the quality of the ecosystem (Hackbarth *et al*., 2015). The main source of environmental pollution with heavy metal ions is industrial activity. Among the metals most commonly used in industries, the most polluting for the environment are lead, mercury, cobalt, cadmium, chromium, nickel and zinc. The development of industrial activities has led to increased emissions of heavy metals in the environment, with negative consequences on soils, plants, rivers and groundwater (Volesky, 2001; Febrianto *et al*., 2009). Therefore, it is necessary to find appropriate methods that should be environmentally friendly and should remove heavy metal ions in a more efficient and cheaper way (Oliveira *et al*., 2013). Traditional methods of removing metal ions are expensive, involve high energy consumption, some methods can cause secondary pollution.

The biosorption process is considered a favourable alternative for removing heavy metal ions from aqueous media. The main advantages of this method are high efficiency even at low concentrations of heavy metals, recycling of biosorbent material, low energy consumption and ease of operation (Kratochvil and Volesky, 1998; Febrianto *et al*., 2009; Wang and Chen, 2009). The materials used as biosorbents in such processes have different advantages, such as the presence of varieties of functional groups (carboxyl, amino, phosphate, phenol, amide and sulfate) that can bind heavy metals from aqueous media (Mungasavalli *et al*., 2007; Ahalya *et al*., 2003).

Marine algae are an abundant and diverse ecosystem that has shown based on studies conducted by researchers, that they are beneficial to the environment. This biomass resource is of great interest in environmental engineering due to its many properties in remedying various environmental problems, such as the ability to decontaminate wastewater, soil decontamination, soil fertilization. In recent years, there has been an increase in the amount of seaweed on beaches, becoming a major problem for local authorities and tourists, which is why several researchers have developed papers and studies to capitalize on this biomass resource to solve this problem. environmental. Unfortunately, studies in the literature (Donmez *et al*., 1999; Romera *et al*., 2007; Bulgariu and Bulgariu, 2014) have shown that the biosorption performance of most marine algae biomass is quite low, and that more many biosorption steps for the quantitative removal of various heavy metal ions.

A solution to increase the efficiency of marine algae biomass in the biosorption processes could be the extraction of active compounds from their structure (such as alginate) and the use of these compounds as biosorbents.

Alginate extracted from seaweed is an organic biopolymer that contains numerous free carboxyl and hydroxyl groups (Kumar and Sahoo, 2017; Latufa *et al*., 2017) that can interact with heavy metal ions in aqueous media compared to functional groups of marine algae biomass Alginate is a polymer that belongs to the polysaccharide family and consists of two monomers: β-D guluronic acid (G) and α-L manuronate acid (M) or both (GGMM) (Truus *et al*., 2001; Soares *et al*., 2004).

In this study, the biosorbent performance of red marine algae biomass and alginate in retaining Zn(II) ions from aqueous solutions was comparatively analysed, as a function of initial Zn(II) ions concentration and contact time. The maximum biosorption capacities, obtained by Langmuir isotherm models and pseudo-second order were compared and the efficiency of these two biosorbent in the removal of Zn(II) ions from aqueous media was detailed discussed.

2. Experimental

2.1. Preparation of Biosorbents

The red marine algae (*Callithamnion corymbosum*) were collected from the Black Sea coast, in August 2016. The collected biomass was washed several times with distilled water to remove impurities and dried in air at 70°C, for 8 hours. After drying, the biomass was crushed and sieved to a particle size of 1.0 – 1.5 mm and stored in desiccators for further use. Alginate was extracted in the basic medium, and the experimental procedure was detailed presented in a previous study (Lucaci and Bulgariu, 2018).

2.2. Chemical Reagents

The zinc stock solution (677.43 mg Zn(II)/L) was prepared from zinc sulphate (Chemical Company, Romania) and dissolved in distilled water. Fresh working solutions were used for each experiment, which was obtained by diluting an exact volume of stock solution with distilled water. A solution of 0.1 N HNO_3 (Chemical Company, Romania) was used to adjust the pH of the initial solution.

2.2. Biosorption Studies

The biosorption performances of red algae and alginate for Zn(II) ions were evaluated using the biosorption capacity (q, mg/g) and the removal percent (R,%) calculated from the experimental results, according to the following equations:

$$q = \frac{c_0 - c}{m} \cdot V \qquad (1)$$

$$R = \frac{c_0 - c}{c_0} \cdot 100 \quad (2)$$

where c_o, c are initial and equilibrium concentration of Zn(II) in solution, V is the volume of the solution and m is the mass of algae or alginate .

The biosorption experiments were performed in batch systems, mixing a constant amount of alginate and marine algae biomass (0.1 g) with volume of 25 mL of known Zn(II) ions concentration, in 150 mL Erlenmeyer flasks, with intermittent stirring. After 24 h, the samples were filtered, and Zn(II) ions concentration was determined spectrophotometrically (VIS Spectrophotometer YA1407020 model) with xylenol orange (λ= 570 nm; 1 cm glass cells, against blank solution), using a prepared calibration graph (Dean, 1995).

The same optimal conditions (initial solution pH of 4.4, biosorbent dose of 2.0 g/L, room temperature) were used in the kinetics experiments, when 25 mL of Zn(II), with the initial concentration of 1 mL per 0.05 g adsorbent, but the contact time between the two phases was varied between 5 and 180 min.

Equilibrium data were analysed using (Ho *et al.*, 1999; Rangabhashiyam *et al*., 2014):

a) Langmuir isotherm model: $$\frac{1}{q} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} \cdot K_L} \cdot \frac{1}{c} \quad (3)$$

b) Pseudo-second order kinetic model: $$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \quad (4)$$

where: q is biosorption capacity*;* q_{max} is the maximum biosorption capacity; K_L is Langmuir constant; q_e,q_t are the biosorption capacities at equilibrium and time t;k_2 is the rate constant pseudo-second order model.

3. Results and Discussions

3.1. FTIR Spectra of Biosorbens Materials

The identification of the main functional groups of marine red algae and alginate was done using FTIR spectra recorded for each material (Fig. 1). The presence of intense absorption bands at: 3440 cm^{-1} (hydroxyl and aliphatic amines), 1639 cm^{-1} (C–O–C bond from carboxylic and carbonyl compounds), 1415 cm^{-1} (C–O–H bonds from alcohols), 1080 cm^{-1} (C–O–C from ethers), indicate that on the surface of both studies materials (marine red algae and alginate are numerous functional groups that can retain metal ions in the aqueous solution, by electrostatic interactions.

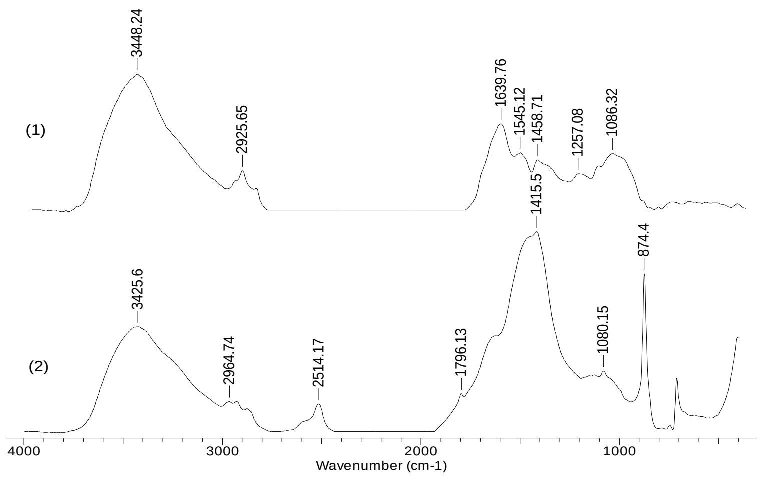

Fig. 1 – FTIR spectrum of marine red algae (1) and alginate (2).

However, these functional groups have degrees of ionization that depend on the experimental conditions, and therefore biosorption studies were performed under the conditions selected as optimal (initial solution pH of 4.4, biosorbent dose of 2.0 g/L, room temperature, 24 hours of contact time).

3.2. Influence of Initial Zn(II) Ions Concentration and Isotherm Modelling

In Fig. 2 illustrates comparatively the biosorptive performances of red marine algae biomass and alginate in the removal processes of Zn(II) ions from aqueous solution.

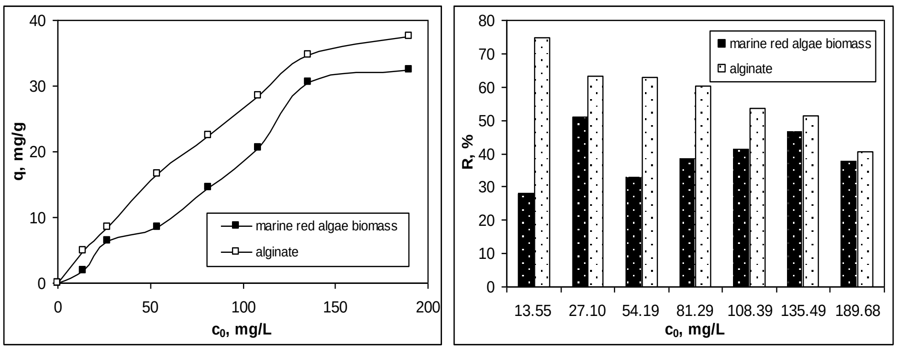

Fig. 2 – Variation of biosorption capacity (*a*) and removal percent (*b*) as a function of initial Zn(II) concentration in studied biosorption processes.

The experimental results from Fig. 2*a* show that the biosorption performances depends: (i) on the initial concentration of Zn(II) ions in aqueous solutions, for both materials studied (in the studied concentration range, the biosorption capacity increases from 1.79 to 32.26 mg/g in case of algae, and from 4.93 to 37.60 mg/g in case of alginate), and (ii) on the nature of biosorbent (at initial Zn(II) ions concentration of 190 mg/L, the biosorption capacity is 32.36 mg/g for marine algae biomass and 37.60 mg/g for alginate).

On the other hand, the influence of the nature of the biosorbent is much more evident from the analysis of the values obtained for the removal percents (Fig. 2*b*). The decrease of these values from 51.05% to 37.52% in case of marine red algae biomass, and from 74.70% to 40.47% in case of alginate, on entire interval of Zn(II) ions concentration, indicates that the alginate is more efficient in the biosorption process, compared with marine red algae biomass.

In order to provide a quantitative description of the biosorption efficiency, the experimental isotherms were analyzed using Langmuir isotherm model. The linear representations of Langmuir model are presented in Fig. 3, while the isotherm parameters are summarized in Table 1.

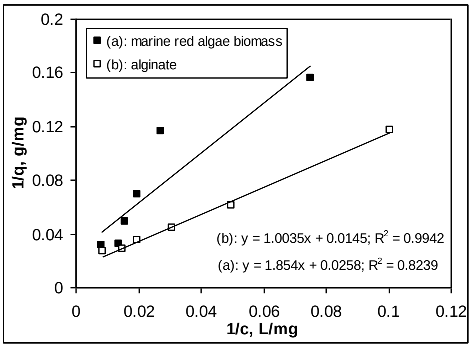

Fig. 3 – Linear representations of Langmuir model for the biosorption of Zn(II) ions on marine red algae biomass and alginate.

Table 1

Isotherm Parameters for Zn(II) Ions Biosorption on Marine Red Algae Biomass and Alginate

Isotherm parameters	Marine red algae biomass	Alginate
q_{max}, mg/g	38.76	68.97
K_L, g/L	0.0139	0.0144
R^2	0.8239	0.9942

As can been observed from Fig. 3 and Table 1, the Langmuir isotherm model well describe the experimental data obtained at Zn(II) ions biosorption on marine red algae biomass and alginate. This means that the retention of

Zn(II) ions occurs at the biosorbent surface until a monolayer coverage is formed (Rangabhashiyam *et al*., 2014). However, the following aspects need to be highlighted: (i) the maximum biosorption capapcity is higher in case of alginate than in case of marine red algae biomass, which means that the alginate is a more efficient biosorbent for Zn(II) ions removal, and (ii) the values of Langmuir constant (K_L, L/g) are close, which suggest that in the retention process of Zn(II) ions, the same types of functional groups are involved in the case of both biosorbents.

3.3. Influence of Contact Time and Kinetic Modelling

The experimental results obtained at the study of the influence of contact time between the biosorbent materials and the aqueous solution containing Zn(II) ions, are presented in Fig. 4. As expected, as the contact time between the two phases of the biosorption system increases, the amount of Zn(II) ions retained per unit mass of biosorbent (q, mg/g) also increases (Fig. 4).

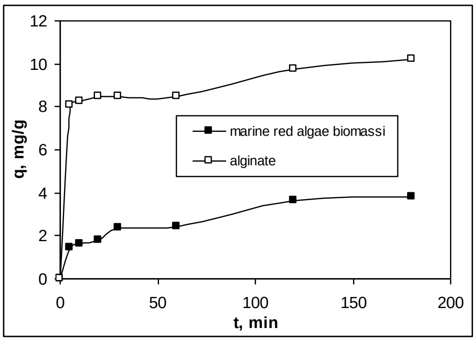

Fig. 4 – Influence of contact time for Zn(II) ions biosorption on marine red algae biomass and alginate.

The biosorption process is very fast in the first 10 min, when more than 63% of Zn(II) ions are retained on alginate, after that become slower near to equilibrium. Unlike alginate, in the case of marine red algae biomass, the removal of Zn(II) ions after 10 min is around 12%, and does not exceed 30% until the end of the experiments. To obtain a quantitative evaluation of the kinetics of biosorption processes, the experimental data were modelled using the pseudo-second order kinetic model. The linear dependences of this model for the biosorption of Zn(II) ions on marine red algae biomass and alginate is illustrated in Fig. 5, and the kinetic parameters are presented in Table 2.

As can be seen from Fig. 4 and Table 2, the pseudo-second order kinetic model accurately describes the experimental data obtained at the biosorption of Zn(II) ions on marine red algae biomass and alginate. This indicates that Zn(II) ion retention occurs mainly through electrostatic interactions, and that they require two favourable binding sites on the biosorbent surface (Ho *et al*., 1999).

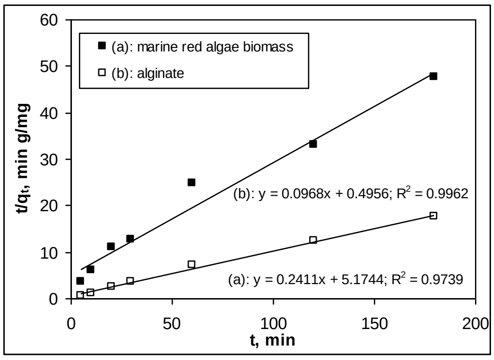

Fig. 5 – Linear representations of the pseudo-second order kinetic model for Zn(II)ions biosorption on marine red algae biomass and alginate.

Table 2
Kinetic Parameter Values of Pseudo-Second Order Model

Biosorbent	Marine red algae biomass	Alginate
q_e, mg/g	4.15	10.33
k_2, g/mg min	0.0465	0.1953
R^2	0.9739	0.9962

An important aspect must be highlighted, namely that the rate constants significantly depending on the nature of the biosorbent. Thus, it can be observed that the rate constant (k_2, g/mg min) is over 4 times higher in the case of alginate compared to the marine red algae biomass (see Table 2). This difference explain why in the case of alginate, Zn(II) ions biosorption reach more quickly the equilibrium state (see Fig. 4), and the biosorption process is more efficient.

4. Conclusions

In this study are evaluated the biosorption performances of alginate compared to marine red algae biomass, to justify the advantage of using such active compounds as biosorbent to retain Zn(II) ions from aqueous solutions. According to the experimental data presented in this study, alginate has a high retention capacity of Zn(II) ions (q_{max} = 68.97 mg/g), almost two times higher than marine red algae biomass (q_{max} = 38.76 mg/g). On the other hand, the kinetic of Zn(II) ions retention on alginate is much faster than in the case of marine red algae biomass. Therefore, through an appropriate selection of experimental conditions, the active compounds extracted from the marine red algae biomass have the potential to become efficient biosorbens for the removal of metal ions from industrial effluents.

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STUDIU COMPARATIV DE BIOSORBȚIE A IONILOR DE Zn(II) DIN SOLUȚIILE APOASE PE BIOMASA DE ALGE MARINE ROȘII ȘI ALGINAT

(Rezumat)

Tendința actuală a cercetărilor de specialitate din bioremediarea mediului este axată pe studiile legate de biosorbția ionilor metalici pe materiale de natură biologică. Algele marine prezintă un mare interes datorită cantității semnificative în care se găsesc sub formă de deșeuri pe plajele noastre românești, motiv pentru care mai mulți cercetători au studiat posibilitatea lor de fi utilizate în procese de remediere a mediului. Conform studiilor de specialitate, dar și în lucrarea de față, se poate observa că algele marine au o capacitate modestă în reținerea ionilor metalici din soluțiile apoase. În compoziția algelor marine se găsesc diverși compuși activi care pot fi separați și utilizați în procesele de îndepărtare a ionilor metalici. Alginatul este un compus activ ce se obține din algele marine. În acest studiu am testat performanțele biosorbtive ale alegelor roșii marine, sp. *Callithamnion corymbosum* și a alginatului extras din acestea, în reținerea ionilor metalici Zn(II) din soluțiile apoase.