

Biosorption of Pb (II) from aqueous solutions by modified of two kinds of marine algae, *Sargassum glaucescens* and *Gracilaria corticata*

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In this research, the batch removal of Pb²⁺ ions from wastewater and aqueous solution with the use of two different modified algae *Gracilaria corticata* (red algae) and *Sargassum glaucescens* (brown algae) was examined. The experiment was performed in a batch system and the effect of the pH solution; initial concentration and contact time on biosorption by both biomasses were investigated and compared. When we used *S. glaucescens* as a biosorbent, the optima conditions of pH, Pb²⁺ concentration and equilibrium time were at 5, 200 mg/L and 70 min, in the range of 95.6% removal. When *G. corticata* was used for this process, pH 3, 15 mg/L pb²⁺ concentration and 50 min contact time, resulted in the maximum removal (86.4%). The equilibrium adsorption data are fitted to the Freundlich and Langmuir isotherm model, by *S. glaucescens* and *G. corticata*, respectively. The pb²⁺ uptake by both biosorbent was best described by the second-order rate model.

Keywords: Biosorption. Lead (II), Removal, *Gracilaria corticata*, *Sargassum glaucescens*, Isotherm mode.

INTRODUCTION

Protection of the environment is a major concern of human communities. Development and various related activities release lots of poisonous materials into the environment and heavy metals are the most dangerous of all¹. Biosorption is a proven technology for the removal of heavy metal ions from synthetic and real industrial effluents. Several researchers investigated numerous biomass types and proposed excellent metal biosorbents including bacteria, fungi, seaweed. Among the most promising biomaterials studied, seaweed was found to be very efficient and binds variety of metals². The biosorption capability of algae has been attributed mainly to the cell wall. Some successfully used and best performed seaweed for cobalt and nickel biosorption include *Ascophyllum nodosum* for cobalt removal and *Sargassum fluitans* for nickel removal. Modeling of biosorption isotherm data is important for predicting and comparing biosorption performance. The two widely accepted for single solute systems are the Langmuir and Freundlich isotherms³. The discharge of metal ions in industrial effluents is of great concern because their presence and accumulation can have toxic or carcinogenic effects on living species. At least 20 metals are classified as toxic, and half of these are emitted into the environment in quantities that show risk factors to human health⁴. Heavy metals are major pollutants that have caused significant environmental problems. Various physical and chemical methods are used for treating heavy metals from industrial wastewater, that include: adsorption, ion exchange, complication, chelating, membrane separation^{5,6}. Different biomass types such as bacteria, fungi and algae have been used to treat wastewater. Biosorption is a term that describes the removal of heavy metals by the passive binding to nonliving microorganisms from an aqueous solution^{7,8}. Marine algae are biological resources which are available in the world. The use of algae, the batch removal of nickel (II) ions from aqueous solution under different experimental conditions using the activated carbon prepared of red alga *Gracilaria*⁹, biosorption of copper from wastewater by the activated carbon preparation

from alga *Sargassum* sp.¹⁰, the batch removal of toxic hexavalent chromium ions from wastewater and aqueous solution using two different activated carbon marine algae *Gracilaria* (red algae) and *Sargassum* sp. (brown algae) were examined. Activated carbon prepared from *Gracilaria* and *Sargassum* sp.¹¹. The use of algae, *Durvillaea pototatorum*, *Ecklonia radiata*¹² *Ascophyllum nodosum*² and *Saccharomyces crevisiae*¹³, *Spirogyra*¹⁴ for heavy metal removal has been reported. In this research, the batch removal of Pb²⁺ ions from wastewater and aqueous solution using by modified two different algae *G. corticata* (red algae) and *Sargassum glaucescens* (brown algae) were examined. The effect of contact time, initial concentration, and pH and equilibrium isotherms on the process was studied.

EXPERIMENTAL

Preparation of biomass

Gracilaria corticata (red algae) and *Sargassum glaucescens* (brown algae) were collected from the Persian Gulf on Queshm Island. Before use, these were washed several times with tap water to remove the sand particles and salts. They were then sun dried for 6 days. The dry biomass was chopped, milled (size fraction of 0.5–1 mm) and then used for biosorption experiments²⁵.

Preparation of Pb²⁺ solution

Stock Pb²⁺ solution (800 mg/L) was prepared by dissolving 0.37 g of pb (CH₃COO)₂ · 3H₂O (Merck) in 250 mL of deionized water. Different concentrations of Pb²⁺ solution were prepared by the dilution of deionized water. The initial pH of sample solution was adjusted with 1M HCl /1 M NaOH using digital pH meter. All the adsorption experiments were carried out at room temperature (23 ± 2 °C)¹¹.

Preparation of Biomass

Red marine macroalgae *G. corticata* and brown algae *S. glaucescens* were used for the removal of pb²⁺ from aqueous solution. They were collected from the Persian

Gulf on Queshm Island, Iran and washed several times with tap water to remove the sand particles and dirt. Then dried for 5 days. The dry biomass was grounded to particle size.

Determination of the Pb²⁺ contents

Concentration of Pb²⁺ in the solution before and after the equilibrium was determined using a Perkin Elmer Analyst 300 atomic absorption spectrometer equipped with a deuterium lamp as the background corrector and an air-acetylene burner, and controlled by an IBM personal computer. The hollow cathode lamp was operated at 15 mA, and the analytical wavelength was set at 324.8 nm.

Adsorption experiments

A series of flasks containing Pb²⁺ solutions varying in the concentration from 10–30 ppm of biomass for *G. corticata* and 50–250 ppm of biomass for *S. glaucescens* were prepared from the stock solution. Adjustment of pH was carried out using 1 N NaOH and 1 N H₂SO₄. Batch equilibrium sorption experiments were carried out in Erlenmeyer flasks for *G. corticata* and *S. glaucescens* were 90 (10–30 ppm of biomass of metal solution) and 70 min (50–250 ppm of biomass, of metal solution) respectively, in a rotary shaker. These experiments were done at pH 1.0–13.0. After the sorption equilibrium was reached (90 and 70 min), the solution was separated from the biomass by membrane filtration. The initial and equilibrium Pb²⁺ concentrations in each flask were determined by atomic absorption spectrometry (AAS). To maximize Pb²⁺ removal by the adsorbent, batch experiments were conducted at a constant temperature using the optimum conditions of all pertinent factors, such as dose, pH, initial concentration, and contact time. Subsequent adsorption experiments were carried out using only the optimized parameters.

Equilibrium isotherm

Lead uptake capacities and sorption isotherm

The amount of metal adsorbed by activated carbon was calculated from the difference between the metal quantity added to the biomass and the metal content of the supernatant using the equation

$$q_e = (C_0 - C_e) V/M \quad (1)$$

where q_e is the metal uptake (mg metal adsorbed per g adsorbent), C_0 and C_e are the initial and equilibrium metal concentrations in solution (mg/L), V is the volume of the solution (mL), and M is the weight of algae marine (g). To examine the adsorbed and aqueous concentration at equilibrium, sorption isotherm models and Langmuir and Freundlich adsorption models were used for the data. These isotherm constants for Pb²⁺ are presented in Table 1.

Freundlich adsorption model

The Freundlich model¹⁵ habitually gives a better fit for adsorption from liquids and can be expressed as

$$q_e = K_f C_e^{1/n} \quad (2)$$

In this model, the rate of adsorption is of the constants $1/n$ and K_f (L/g). For a good adsorbent, $0.2 < 1/n < 0.8$,

Table 1. The isotherm parameters obtained for the biosorption of Pb²⁺

Isotherm model	<i>S. glaucescens</i>	<i>G. corticata</i>
Langmuir		
Q _m (mg/g)	-6.56	0.761
b (L/mg)	-0.0479	5.43
R ²	0.487	0.999
Freundlich		
1/n	1.587	0.1535
K _f (mg/g)(L/mg) ^{1/n}	0.163	0.569
R ²	0.883	0.6294

and a smaller value of $1/n$ shows better adsorption and formation of a rather strong bond between the adsorbate and the adsorbent. Many researchers have used this model to interpret this sorption data for various systems^{16–19}.

Langmuir adsorption model

The most widely used isotherm equation for modeling equilibrium is the Langmuir equation. It is assumed that there is a finite number of binding sites that are homogeneously shared over the adsorbent surface. These binding sites have the same adsorption of a single molecular layer, and there is no interaction between adsorbed molecules. The saturated monolayer isotherm can be represented as

$$q_e = b q_{\max} C_e / (1 + b C_e) \quad (3)$$

where q_e is metal ions adsorbed (mg/g), C_e is the equilibrium concentration (mg/L), q_{\max} is the maximum adsorption capacity, and b is an affinity constant; q_{\max} represents a practical limiting adsorption capacity when the surface is fully covered with metal ions and assists in the comparison of adsorption performance, in the cases where the sorbent did not reach its full saturation in experiments and b is constantly related to the affinity of the binding sites²⁰.

Adsorption kinetic studies

The kinetics of adsorption describes the rate of lead ion uptake on the prepared from *G. corticata* and *S. glaucescens*, which controls the equilibrium time. These kinetic models included the first-order and second-order equations.

Pseudo first-order model

The pseudo first-order rate expression is described by the equation

$$dq_t/dt = k_1 (q_e - q_t) \quad (4)$$

where q_e is lead adsorbed at equilibrium per unit weight of the sorbent (mg/g), q_t is copper adsorbed (mg/g), and k_1 is the rate constant (min⁻¹)²⁰. The integrated form of Eq. (4) becomes

$$\log (q_e - q_t) = \log (q_e) - (k_{1/2.303})t \quad (5)$$

A plot of $\log (q_e - q_t)$ versus (t) indicates a straight line of slope $(k_{1/2.303})$ and an intercept of $\log (q_e)$.

Pseudo second-order model

The sorption data also analyzed a pseudo second order (Ag and Aktay 2002), given by:

$$dq_t/dt = K_2 (q_e - q_t)^2 \quad (6)$$

where K_2 is the equilibrium rate constant (g/mg, min), and q_e and q_t are the sorption capacities at equilibrium and at time t . The integrated form of Eq. (5) becomes

$$1/(q_e - q_t) = 1/(q_e) + K_2 t \quad (7)$$

which has a linear form:

$$t/q_t = 1/K_2 q_e^2 + (1/q_e)t \quad (8)$$

A plot t/q_t versus t shows a straight line of slope $(1/q_e)$ and an intercept of $(1/K_2 q_e^2)^{21}$.

In this study, the batch method was used for the biosorption of lead by *G. corticata* and *S. glaucescens*.

Statistical Analysis

Error bars are indicated wherever necessary. All statistical analysis was done using SPSS12 for windows. The statistical significance of differences among the values was assessed by using the one-way ANOVA test.

RESULTS AND DISCUSSION

The present study shows biosorption of Pb^{2+} ions by two kinds of modified marine algae *G. corticata* (red algae) and *S. glaucescens* (brown algae) biomass from aqueous solutions was investigated. The data obtained from this work supports the view that the *S. glaucescens* is an effective and low-cost adsorbent for the removal of Pb^{2+} from aqueous solutions. The adsorption of metal ions is dependent on *S. glaucescens*, concentration of metal ions, retention time, and pH of the metal solution.

Effect of contact time

To find the suitable equilibrium time of the biosorption, an experiment was carried out at different time intervals

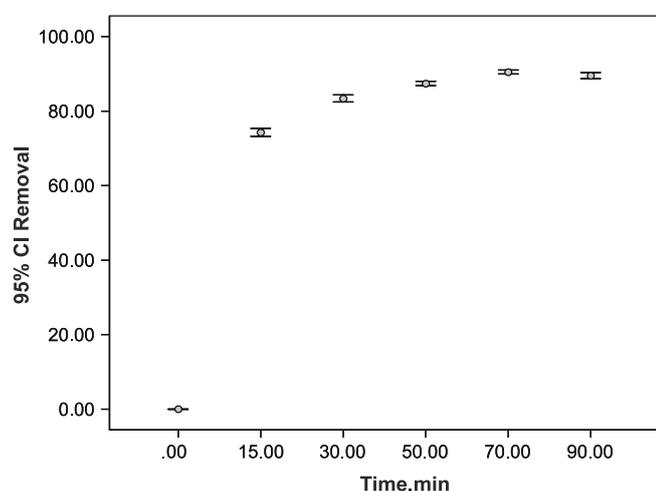


Figure 1a. Biosorption of 100 ml Pb^{2+} solution, 100 and 25 mg/L, by *Sargassum glaucescens* 200 rpm shaking rate in different times

(15, 30, 50, 70 and 90 min). As it can be seen in figure 1 with the beginning of the process, the uptake of Pb ions increased quickly and after 70 and 50 min for the 100 and 25 mg/L of Pb^{2+} solution, the exchange ion became slow, by *S. glaucescens* and *G. corticata*, respectively. It seems that, *S. glaucescens* is more effective in the removal of high concentration of lead solution.

Optimum contact time for both the dried and activated carbon biosorbent was found to be 120 min. In previous literature, similar findings have been reported by the evaluation of the marine alga *G. corticata* for the adsorption of Cu (II) from wastewater in a packed column²².

Effect of initial concentration

The initial concentration of metal ions provides an important driving force to overcome all mass transfer resistances of metal ions between the aqueous and solid phases⁹. The influence of metal ion concentration on the biosorption by *S. glaucescens* and *G. corticata* has been shown in figure 2a and figure 2b respectively.

As it can be seen, by increasing the initial concentration, the removal percent was increased by using *S. glaucescens* and the maximum removal of Pb^{2+} ions, after 70 min was 200 mg/L in the range of 89.11%. As shown in figure 2b, the removal of Pb^{2+} ions by *G. corticata* was decreased, by increasing metal concentration and the maximum removal after 50 min was 15 mg/L in the range of 99.2%. Thus *S. glaucescens* is useful for the removal of high concentrations of Pb^{2+} . In recent studies, biosorption of Ni (II) with 30, 50 and 70 mg/L, by *G. corticata*, after 60 min was in the ranges of 99.03, 97.99 and 95.12%⁹. And *G. corticata* was used for the

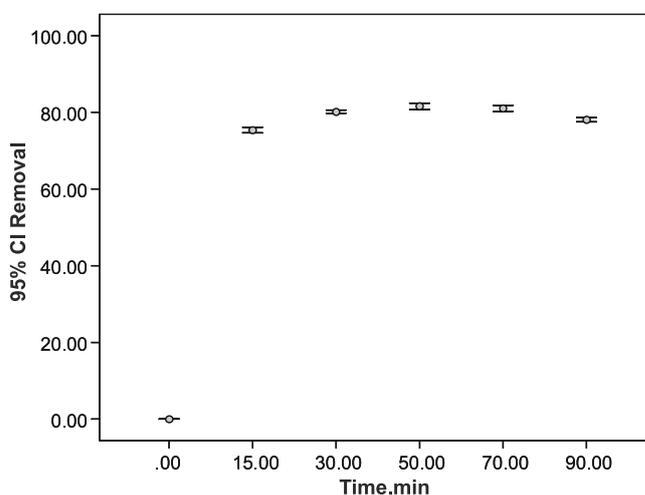


Figure 1b. Biosorption of 100 ml Pb^{2+} solution, 100 and 25 mg/L, by *Gracilaria corticata* 200 rpm shaking rate in different times

	Sum of squares	df	Mean square	F	Sig.
Between groups	30995.665	5	6199.13 3		
Whiten groups	8.715	24	0.36 3	17070.68 3	0.00 0
Total	31004.381	29			

Table 3a. Anova variance statistical analysis; Biosorption of 100 ml Pb^{2+} solution at different metal concentration, 200 rpm shaking rate by *Sargassum glaucescens* during 70 min.

	Sum of squares	df	Mean square	F	Sig.
Between groups	548.188	4	137.047		
Whiten groups	7.383	20	0.36 9	371.26 2	0.00 0
Total	555.571	24			

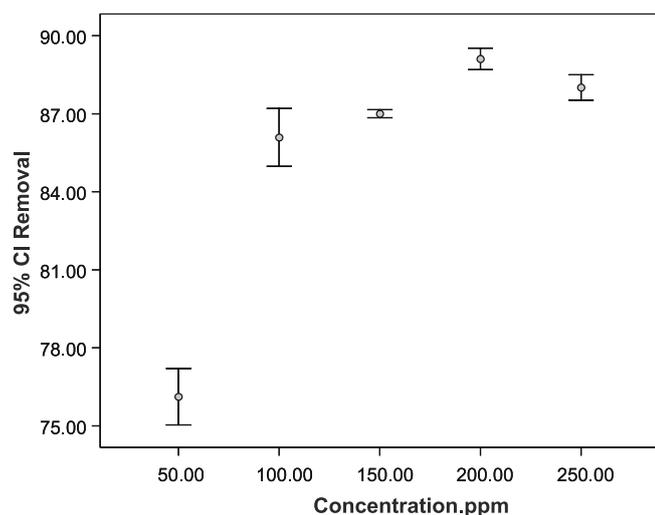
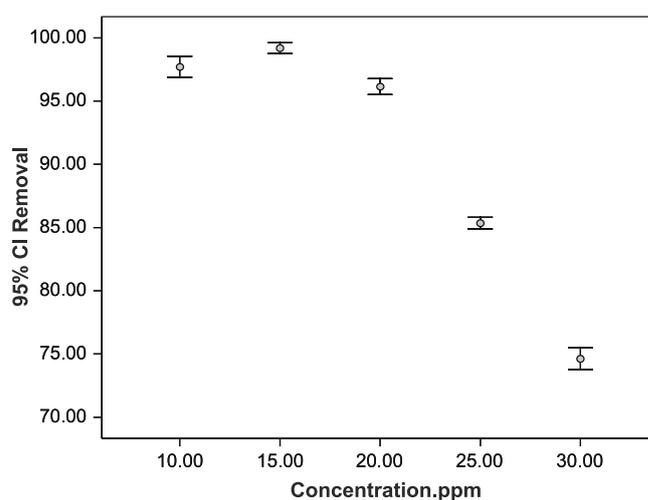
Table 3b. Anova variance statistical analysis; Biosorption of 100 ml Pb^{2+} solution at different metal concentration, 200 rpm shaking rate by *G. corticata* during 50 min.

Table 4a. Anova variance statistical analysis; Biosorption of 100 ml Pb²⁺ solution at different initial pH, 200 rpm shaking rate 200 ppm Pb²⁺ solution by *Sargassum glaucescens* in 70 min.

	Sum of squares	df	Mean square	F	Sig.
Between groups	548.188	4	137.047	371.26 2	0.00 0
Whiten groups	7.383	20	0.36 9		
Total	555.571	24			

Table 4b. Anova variance statistical analysis; Biosorption of 100 ml Pb²⁺ solution at different initial pH, 200 rpm shaking rate 15 ppm Pb²⁺ solution by *G. corticata* in 50 min.

	Sum of squares	df	Mean square	F	Sig.
Between groups	2189.063	4	547.266	1917.204	0.00 0
Whiten groups	5.709	20	0.285		
Total	2194.772	24			

**Figure 2a.** Biosorption of 100 ml Pb²⁺ solution at different metal concentration, 200 rpm shaking rate by *Sargassum glaucescens* during 70 min**Figure 2b.** Biosorption of 100 ml Pb²⁺ solution at different metal concentration, 200 rpm shaking rate by *Gracilaria corticata* during 50 min

biosorption of 180 mg/L Cu (II) solution in a packed column in the range of 80%²².

Effect of pH on adsorption

The initial pH of the metal solution is an important parameter affecting adsorption of metal ions²³. The effect of solution pH on biosorption was studied at room temperature by varying the pH. Results have been shown in figure 3a and figure 4b.

When *S. glaucescens* has been used for pb²⁺ ion biosorption, significant difference, was not observed in the removal percent, by the changes of pH from 3 to 13. But, the changes of pH values from acidic to basic conditions decreased the pb²⁺ removal by using *G. corticata* as a biosorbent. At least, for both *S. glaucescens* and *G. corticata*, maximum removal of pH occurred in acidic conditions: pH 3 and pH 5 in the range of 95.6 and 86.4%, respectively. Actually, in basic conditions, the groups of biosorbent could uptake fewer pb²⁺ ions.

Kadirvelu *et al*, obtained maximum removal of heavy metals pb (II), Cd (II), Ni (II) and Cu (II), by increasing pH from 2 to 6 and using activated carbon prepared from an agricultural soil waste²⁴ Gupta *et al*, obtained maximum biosorption of chromium (VI) by green algae *Spirogyra* species in optimum pH of 2⁴⁴.

Adsorption isotherm

Adsorption isotherms are important for the description of how an adsorbate will interact with an adsorbent and are critical in the use of adsorbents. Equilibrium studies on adsorption isotherms are characterized by certain constants whose values express the surface properties and affinity of the adsorbent. Equilibrium between the adsorbent and the adsorbate is described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in the solution at a fixed temperature (23 ± 2°C), at equilibrium. To study the adsorption isotherm, two models were analyzed.

	Sum of squares	df	Mean square	F	Sig.
Between groups	3527.586	4	881.896	5931.108	0.00 0
Whiten groups	2.974	20	0.149		
Total	3530.560	24			

Table 5a. Kinetic modeling biosorption by *Sargassum glaucescens*, second-order kinetic model

	Sum of squares	df	Mean square	F	Sig.
Between groups	701.158	4	175.290	425.212	0.00 0
Whiten groups	8.245	20	0.412		
Total	709.403	24			

Table 5b. Kinetic modeling biosorption by *Gracilaria corticata*, second-order kinetic model

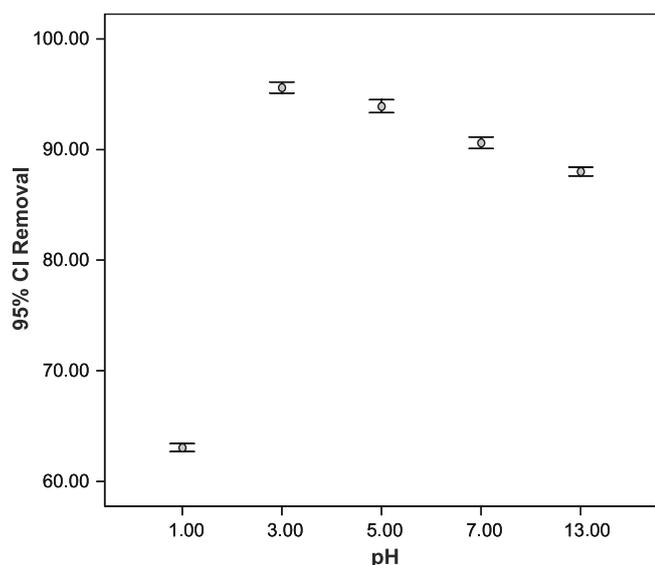


Figure 3a. Biosorption of 100 ml Pb^{2+} solution at different initial pH, 200 rpm shaking rate 200 ppm Pb^{2+} solution by *Sargassum glaucescens* in 70 min.

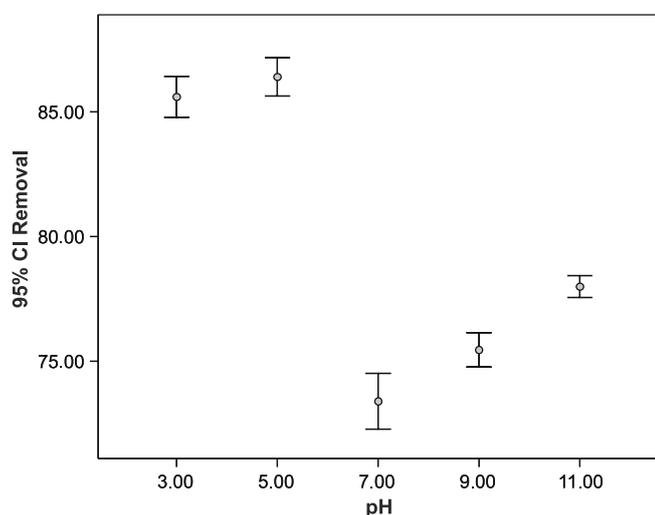


Figure 3b. Biosorption of 100 ml Pb^{2+} solution at different initial pH, 200 rpm shaking rate 15 ppm Pb^{2+} solution by *Gracilaria corticata* in 50 min.

Langmuir and Freundlich isotherms

The Langmuir adsorption isotherm is the most widely applied adsorption isotherm. A basic assumption of the Langmuir theory is that adsorption takes place at specific homogeneous sites within the adsorbent. The applicability of the empirical Freundlich isotherm was also analyzed based on the sorption on a heterogeneous surface, using the same set of experimental data of dried brown algae and its activated carbon. The isotherm experimental results showed that the data could be well modeled according to the Langmuir and Freundlich adsorption isotherm (Figure's 4a and 4b).

The Langmuir constant (q_{max}) is dependent on experimental conditions such as solution pH. Another importance in evaluating the sorbent performance is the initial gradient of the adsorption isotherm, since it indicates the sorbent affinity at low metal concentrations. In the Langmuir equation, this initial gradient corresponds to the affinity constant. As we can see from Table 1 the data could be well modeled according to either the Langmuir or Freundlich adsorption isotherm. In previous investigations, a similar method using the

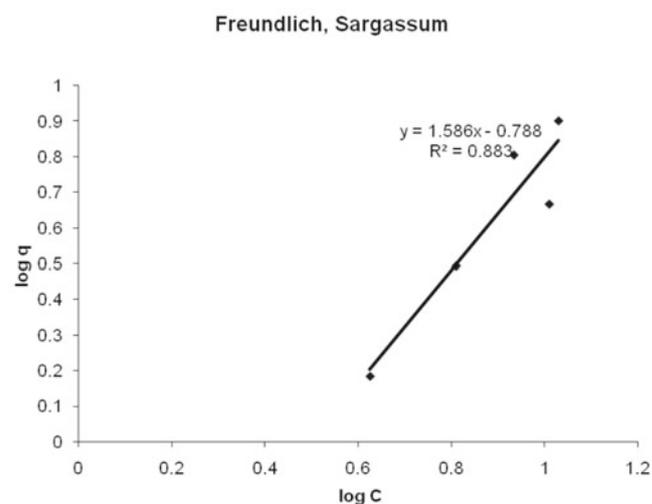


Figure 4a. The isotherm models biosorption by *Sargassum glaucescens*, the Freundlich model

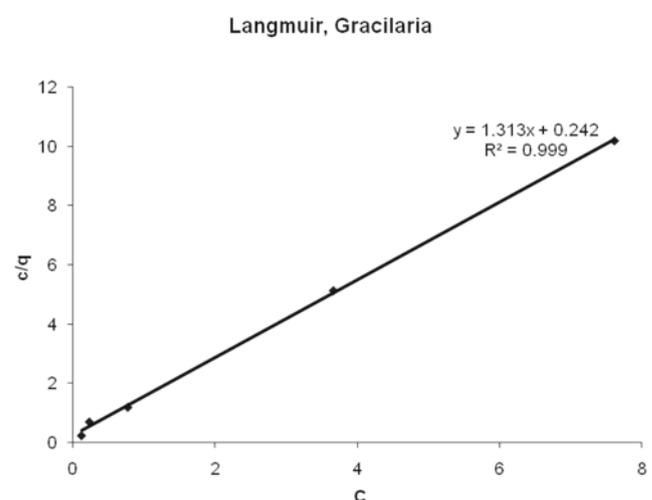


Figure 4b. The isotherm models biosorption by *Gracilaria*, the Langmuir model

marine algae *Gracilaria* for the biosorption of Ni (II) has been reported⁹.

Kinetic modeling

The second and first-order rate constant ($k_{1,ads}$) and q_e determined from the model indicated that this model failed to estimate q_e since the experimental values of q_e differed from those estimated in Table 2 and figure's 5a and 5b.

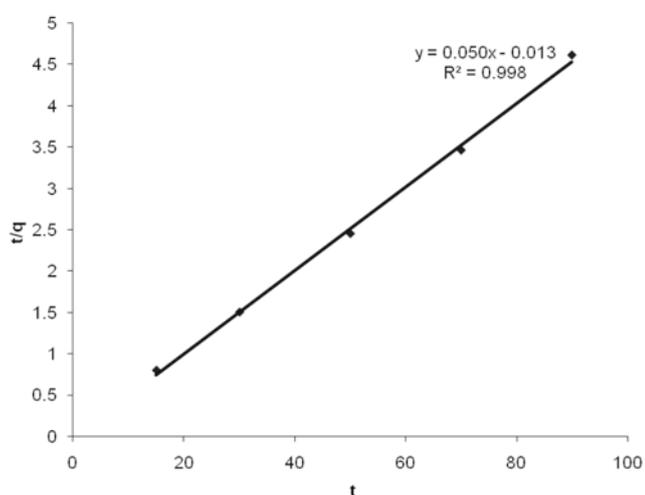
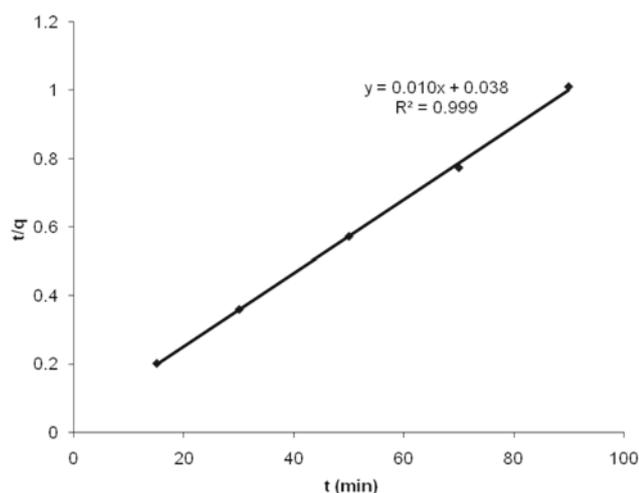
Subsequently, the rate of uptake of Pb^{2+} onto the biomass increased quickly to 70 and 90 min, and no further adsorption was observed beyond this period. The Pb^{2+} uptake by the biosorbents was best described by the pseudo second-order rate model. The pseudo second-order model is based on the supposition that adsorption follows a second order, which means the rate of occupation of adsorption sites, is proportional to the squares of the number of unoccupied sites¹⁹. In previous literature for the evaluation of the AC prepared from the algae *Gracilaria* for the adsorption of Cu (II) the adsorption follows the second-order rate expression⁹.

Adsorption equilibrium

The isotherm experimental results showed that the data could be well modeled according to the Langmuir adsorption isotherms (figure's 4a and 4b). The Langmuir

Table 2. The parameters obtained for the first and second-order kinetic model by two biosorbent

Algae	C_0, pb^{2+}	K_1	q_e (first-order)	R^2	K_2	q_e (second-order)	R^2
<i>S. glaucescens</i>	100	0.00092	1.64	0.692	0.003	93.5	0.999
<i>G. corticata</i>	25	0.00046	1.40	0.1345	0.183	19.8	0.998

**Figure 5a.** Kinetic modeling biosorption by *Sargassum glaucescens*, second-order kinetic model**Figure 5b.** Kinetic modeling biosorption by *Gracilaria corticata*, second-order kinetic model

constant (q_{\max}) is dependent on experimental conditions such as solution pH. Another important factor in evaluating the sorbent performance is the initial gradient of the adsorption isotherm, since it indicates the sorbent affinity at low metal concentrations. In the Langmuir equation, this initial gradient corresponds to the affinity constant. The Freundlich and Langmuir isotherm constants were obtained and are presented in Table 1.

CONCLUSION

In this study, adsorption of pb^{2+} on two Marine algae *G. corticata* (red algae) and *Sargassum glaucescens* (brown algae) has been studied. These treated biomass could be used as a low cost adsorbent for the removal of pb^{2+} from aqueous solution. The adsorption of metal ions is dependent on the amount of concentration of pb^{2+} , pH and retention time. The adsorption rate would be increased by increasing time to 70 and 50 min by *S. glaucescens* and *G. corticata*, respectively. The results showed that *S. glaucescens* is more effective for the

removal of pb^{2+} , in optimum conditions of the process in the range of 95.6%. *Gracilaria* has adsorbed pb^{2+} , in optimum conditions in the range of 86.4%. The equilibrium adsorption data by *S. glaucescens* and *G. corticata* are correlated to the Freundlich and Langmuir isotherm equation, respectively, and can be described by the second-order kinetic models.

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