Kinetic, thermodynamic and structural study of the biosorption of lead and cadmium by red macroalga (*Ceramium virgatum*)

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Abstract: In this study a red macroalga *Ceramium virgatum* has been classified and used for removal of Cd(II) and Pb(II) from aqueous mediums. The effects of pH, adsorbant concentration, contact time and temperature on biosorption process were studied in batch experiments. Langmuir and Freundlich models were applied to describe the biosorption isotherm of the metal ions by *C. virgatum* biomass. The biosorption data were well described by Langmuir than Freundlich isotherm. The monolayer biosorption capacity of *C. virgatum* biomass for Pb(II) and Cd(II) ions was found to 53.9 mg.g^{-1} and 51.6 mg.g^{-1}, respectively. The mean free energy calculated from Dubinin-Radushkevitch isotherm indicate that the biosorption of Pb(II) and Cd(II) onto *C.virgatum* macroalga was taken place by chemical sorption. The thermodynamic studies showed that the biosorption was spontaneous and exothermic in nature. Kinetics data of both metal ions were best described by pseudo second order model. The analysis with FTIR indicated that the carboxyl (-CO), hydroxyl (-OH), and amine (-NH) groups are responsible for binding of metal ions. Desorption experiment of metallic ions gives a high regeneration yield (over 90 %) reached after three sorption/desorption cycles showing a good reusability of the biomass.

Keywords : Red macroalga, lead and cadmium, biosorption, desorption.

INTRODUCTION

Heavy metals represent the major part of inorganic polluants and should be usually removed from aqueous medium. Some of them, such as lead (Pb) and cadmium (Cd) are highly toxic and they do not have any biological utility [1]. They are very toxic and cancerogenic in nature [2]. The ions released from lead and cadmium are cumulative poisons capable of being assimilated and stored in the tissues of organisms, causing noticeable adverse physiological effects. Cd(II), which is widely used and extremely toxic in relatively low dosage, is one of the principle heavy metals responsible for causing renal disorder, kidney damage, bone fraction and destruction of red blood cells [3]. Lead is the most significant toxin of the heavy metals because it was used for a long time as anti-knock in gasolines. Inorganic forms of lead cause irreversible brain damage, kidney disease and typically affect cardiovascular and reproductive systems. Moreover organic lead toxicity tends to affect the central nervous system. Therefore, the removal of these toxic metal ions from water prior to supplying water for drinking, bathing and vegetables irrigation is very important and crucial.

Several processes such as ion exchange, precipitation, ultrafiltration, reverse osmosis and electrodialysis have been used for the removal of heavy metal ions from aqueous mediums [4]. However, the feasibility of these processes is sometimes limited by many economic and technical factors. Biosorption represent another way for wastewater treatment which draw a much attention in the recent years. It has been found to be an economically feasible and easily to doing for the metal ion removal from aqueous solutions. Basically, it can be based on the following mechanisms: physical or chemical adsorption, ion exchange, and complexation.

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Among the different biological substrate studies, algal biomass have received a great attention due the low sensitivity to environmental and impurity factors, cost saving and its elevated adsorption capacity relatively to activated carbon and synthetic ion exchange resins.

Ceramium virgatum is a red algae grows on rocks to the open shore near to lower water level. This algae is widespread along the shores of Tunisia, grows well along the Mediterranean sea coasts.

The main purpose of this work was to evaluate the potential of *Ceramium virgatum*, for the biosorption of lead and cadmium from aqueous solutions. The effect of pH values, contact time, adsorbent dosage and temperature, were studied subsequently. During this work program, raw and metal-loaded algal biomasses were analyzed with Fourier Transform Infrared spectrometer (FTIR) to assess the functional groups that might involved in the sorption process of both metal ions. Biomass algal will be reused many times consecutively to remove metal ions from water in order to assess the efficiency of the biosorbent after a given adsorption cycle. These results would contribute to a better understanding of the absorption phenomena and help in the development of potential biosorbents using local materials, which possess high capacity for heavy metal uptake and good ability to be regenerated.

MATERIALS & METHODS

The raw biomass of *Ceramium virgatum* was harvested from the cap Zbib beach (North coast of Tunisia). The samples were washed with copious quantities of deionised water to remove extraneous materials as well as release common ions (e.g., Na^+ and Ca^{2+}) present in seawater. The washed biomass was dried at 60 °C for 48 hours. The dried alga biomass was chopped, sieved and the particles with an average of 0.5 mm were used for biosorption experiments.

Stock metal solutions at various concentrations were prepared by dissolving lead nitrate and cadmium nitrate (Analytical reagent grade, Sigma-Aldrich). pH of the solutions was measured by 5500 EUTECH pH- meter using glass electrode calibrated with standard buffer solutions. pH of the solution was adjusted by adding 0.1 $mol.L^{-1}$ HNO_3 and 0.1 $mol.L^{-1}$ NaOH solutions as per required pH value. The metal concentrations were measured using an atomic absorption spectrometer (SHIMADZU AA-680, Japan). FTIR spectroscopy was used to detect vibration frequency changes in the algal sorbent. The spectra were collected by a SHIMADZU 8400 spectrometer within the range 400-4000 cm^{-1}. Raw and metal-loaded algal biomass were analysed at the solid state in KBr pellets. The background obtained from the scan of pure KBr was automatically subtracted from the sample spectrum.

Biosorption processes were carried out using batch method. In order to optimize the experimental conditions, the batch studies were performed for different metal concentrations (10-100 $mg.L^{-1}$), contact time (5-90 min), pH(2-8), biosorbent dosage (1-20 $g.L^{-1}$) and temperature (20-50 °C). The solutions (25 mL of 10 $mg.L^{-1}$) including the metal ions and biosorbent were shaken during optimum contact time in an electrically thermostatic reciprocating shaker (Multimatic-55 model, Selecta Company, Spain) at 120 rpm. After that, the content of the flask was filtered through 0.25 µm Whatman filter paper, and the metal concentration of filtrate was determined using atomic absorption spectrometry. The percent biosorption of metal ion was calculated as following:

$$\text{Biosorption}(\%) = \frac{(C_i - C_e)}{C_i} \times 100 \quad (1)$$

where C_i and C_e are initial and final (or equilibrium) metal ion concentrations, respectively.

All the investigations were carried out in triplicate to avoid any discrepancy in experimental results, with the reproducibility of ± 0.5 and the relative standard deviation of the order of ± 2 %.

RESULTS & DISCUSSION

The biosorption capacity of the alga strongly depends on equilibrium solution pH, so characterization of its effect on adsorption studies is necessary for an accurate evaluation of equilibrium parameters. The biosorption of Pb(II) and Cd(II) was studied over a pH range of 2-8 and the results are given in Fig.1. The biosorption efficiency was increased from 60 % to 96 % for Pb(II) and from 52 % to 95 % for Cd(II) ion as pH was increased from 2 to 5 units. The maximum biosorption was found to be 98 % for Pb(II) and 96 % for Cd(II) ions at pH 5.5. Therefore, all the biosorption experiments were adjusted at this pH value. The biosorption mechanisms on the biomass surface reflect the nature of the physicochemical interaction between the species in solution and the

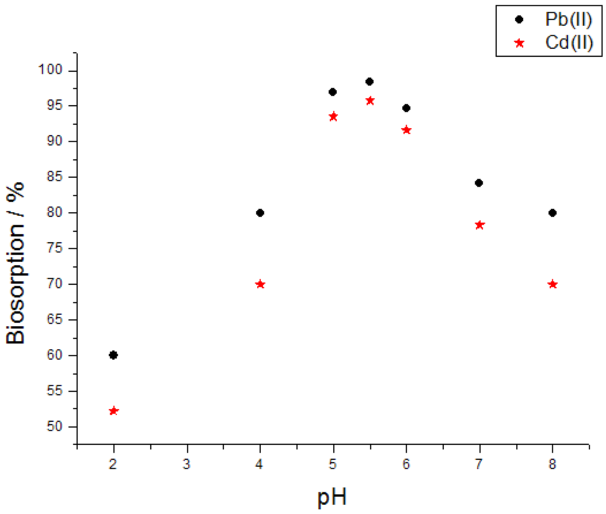

Figure 1. Effect of pH on the biosorption of Pb(II) and Cd(II) onto *Ceramium virgatum.*
(Initial concentration : 10 mg. L^{-1} ; temperature: 20°C ; biomass concentration: 4 g. L^{-1})

biosorptive sites of sorbent. At highly acidic medium (pH < 2.0), the overall surface charge on the active sites became positive and there will be competitively between metal cation and protons on the binding sites of cell wall, which result in lower uptake of metal. The biosorption surface was more negatively charged as the pH of solution increased from 2 to 5.5 units. The functional groups of the biomass were more deprotonated and thus available for the metal ions. Especially, carboxyl, amine and hydroxyl groups are important functional groups involved in biosorption of heavy metals [5]. Decrease in biosorption yield at higher pH (pH > 5.5) is related to the formation of soluble complexes of the metal ion (lead ion in the form of $Pb(OH)^+$, $Pb(OH)_2$, $Pb(HCO_3)_2$, $PbCO_3$ and cadmium ion in the form of $Cd(OH)_2$) which could not be adsorbed by the biosoptive sites on the biomass surface.

The biomass concentration is another important variable during metal uptake. At a given equilibrium concentration, the biomass takes up more metal ions at lower than at higher cell densities [6]. It has been suggested that electro-static interactions between cells can be a significant factor in the relationship between biomass concentration and metal sorption. In this connection, at a given metal concentration, the lower the biomass concentration in suspension, the higher will be the metal/biosorbent ratio and the metal is retained by sorbent 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 low metal uptake comparatively with lower biomass concentrations.

The effect of biomass concentration on the biosorption of Pb(II) and Cd(II) ions was studied using different biomass concentrations in the range 0.1-20 g. L^{-1}. Results showed that the biosorption yield steeply increases with concentration as the biomass concentration was increased from 0.1 to 4 g. L^{-1}. The maximum biosorption percentage reached 98 % for Pb(II) and 96 % for Cd(II) as biomass concentration was 4 g. L^{-1} and it was almost same at higher concentration. This trend could be explained as a consequence of a partial aggregation of biomass at higher biomass concentration, which results in decrease in effective surface area for the biosorption. Therefore, the optimum biomass dosage was selected as 4 g. L^{-1} for further experiments.

Previous works showed that the sorption of heavy metal ions by algae followed a tow-steps mechanism where the metal ion was physically/ chemically bonded onto the surface of the alga before being taken up biologically into the cell [7]. The first step, known as a passive transport, took place quite rapidly, i.e. within 20-30 min whilst the second biological step or active transport, could take much longer time in order to be completed. In this case, since the alga was dried and the biological functions were no longer active, the sorption could only take place on the surface of the cell. Therefore the sorption equilibrium took place quickly within 20 min and no further sorption was observed thereafter.

The rate of biosorption is important for designing batch biosorption experiments. Therefore the effect of contact time on the biosorption of Pb(II) and Cd(II) was investigated. The biosorption yield of Pb(II) and Cd(II) increased considerably until the contact time reached 60 min. Further increases in contact time did not enhance the biosorption yield, so, the optimum contact time was selected as 60 min for further experiments.

On the other hand, the biosorption yield decreased from 98 % to 90 % for Pb(II) and from 95 % to 88 % for Cd(II) as temperature was increased from 20 to 50 °C during the optimum time 60 min. These results indicate the exothermic nature of biosorption onto *Ceramium virgatum*. A decrease in the biosorption of Pb(II) and Cd(II) ions with the rise in temperature may be due to either the damage of active binding sites in the biomass, or increasing tendency to desorb metal ions from the cell wall to the solution. The optimum temperature was selected as 20 °C for further biosorption experiments.

To find out the mechanistic parameters associated with lead and cadmium biosorption, the result obtained by the biosorption experiments were analyzed by Langmuir, Freundlich and Dubinin-Radushkevich models. The theoretical adsorption isotherm of Langmuir is best known among the all isotherm models. It describes the adsorption of solute from a liquid solution on the surface of solid material, assuming monolayer adsorption onto a surface with a finite number of identical sites [8]. This model is represented as follows:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \qquad (2)$$

Where q_e is the equilibrium metal ion concentration on the biosorbent (mg.g^{-1}), C_e is the equilibrium metal ion concentration in the solution (mg.L^{-1}), q_{max} is the monolayer biosorption capacity of the biosorbent (mg.g^{-1}), and K_L is the Langmuir biosorption constant (L.mg^{-1}).). The Linear form of isotherm can be presented as the following :

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \qquad (3)$$

Figure.2 represents for each metal ion the linear curve of $\frac{C_e}{q_e}$ against C_e and data obtained with the correlation coefficient (r) were listed in Table I.

The Freundlich adsorption isotherm is an empirical equation based on the adsorption on the heterogeneous surface [9]. The nonlinear form of the Freundlich adsorption isotherm can be defined by the following equation:

$$q_e = K_F C_e^{1/n} \qquad (4)$$

The Freundlich isotherm constant n is an empirical parameter that varies with the degree of heterogeneity and K_F is related to adsorption capacity. K_F and 1/n values were determinate in using the linear form of Freundlich isotherm described by the following equation :

$$\ln(q_e) = \ln(K_F) + 1/n \ln(C_e) \quad (5)$$

Figure.3 represents for each metal ion the linear curve of $\ln(q_e)$ versus $\ln(C_e)$. The values for Freundlich constants and correlation coefficient (r) for the biosorption process are also given by Table I.

Table I shows that the experimental data are better fitted to Langmuir (r = 0.999 for each metal ion) than Freundlich (r = 0.970 and 0.981 for Pb(II) and Cd(II) respectively) adsorption isotherm.

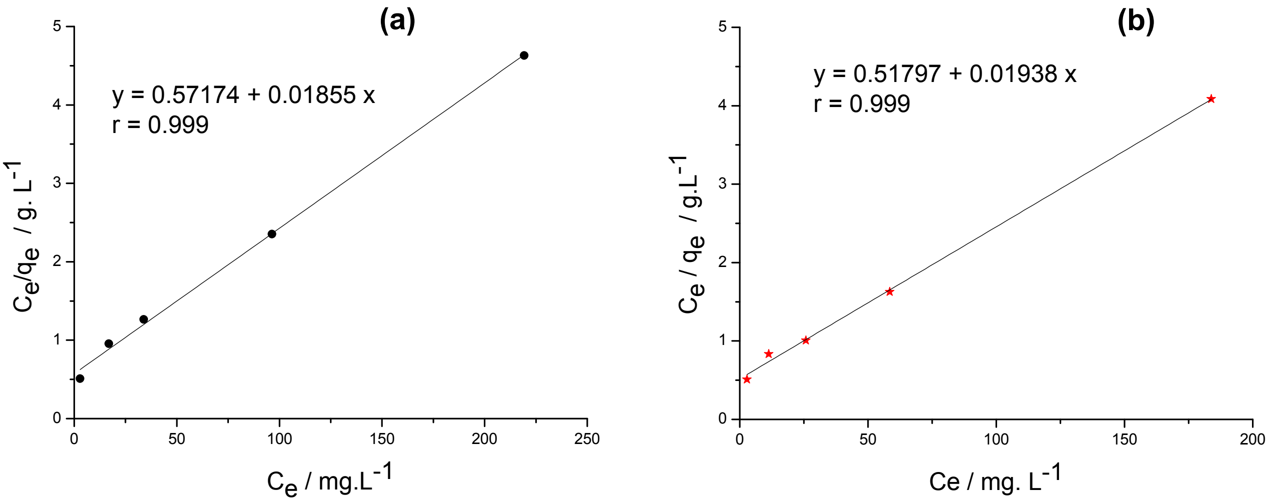

Figure 2. Linear form of Langmuir isotherm for the biosorption onto *Ceramium virgatum*.
(a) for Pb(II) biosorption ; (b) for Cd(II) biosorption
(*Biomass concentration: 4 g.L^{-1}; contact time: 60 min ; pH : 5.5 ; temperature: 20°C)*

Table I. Adsorption isotherm parameters for Cd(II) and Pb(II) biosorption onto *Ceramium virgatum.*

Metal	Langmuir constants			Freundlich constants		
	q_{max} (mg.g^{-1})	K_L (L.mg^{-1})	r	K_F	n	r
Pb(II)	53.9	0.032	0.999	16.3	0.512	0.970
Cd(II)	51.6	0.037	0.999	15.3	0.516	0.981

The equilibrium data were also subjected to the Dubinin-Radushkevich (D-R) isotherm model to determine the nature of biosorption processes as physical or chemical. The D-R isotherm model is more general than Langmuir isotherm, as its concept is not based on ideal assumptions such as equivalence of the sorption sites, absence of steric hindrance between adsorbed and incoming particles, and surface homogeneity on microscopic level [10].

The linear presentation of the D-R isotherm equation [11,12] is expressed by :

$$\mathrm{Lnq_e} = \mathrm{Lnq_m} - \beta\varepsilon^2 \qquad (6)$$

where q_e is the amount of metal ions adsorbed per unit weight of biomass (mol.g^{-1}), q_m is the maximum biosorption capacity (mol.g^{-1}), β is the activity coefficient related to biosorption mean free energy (mol^2.J^{-2}) and ε is the Polanyi potential.

$$\left[\varepsilon = RTLn\left(1 + \frac{1}{C_e}\right)\right] \qquad (7)$$

The D-R isotherm model well fitted the equilibrium data since the linear correlation value was found to be 0.995 for each metal biosorption (Fig.4). The biosorption mean energy (E, kJ.mol^{-1}) is calculated as follow:

$$\mathrm{E} = \frac{1}{\sqrt{2\beta}} \qquad (8)$$

The mean free energy (E, kJ.mol^{-1}) value gives information about adsorption mechanism, physical or chemical. If it lies between 8 and 16 kJ.mol^{-1}, the adsorption process took place chemically and while E < 8 kJ.mol^{-1}, the adsorption process took place physically [13]. The mean free energy was calculated as 10.4 and 10.1 kJ.mol^{-1} for Pb(II) and Cd(II) ions respectively. These results suggest that the biosorption processes of both metal ions onto

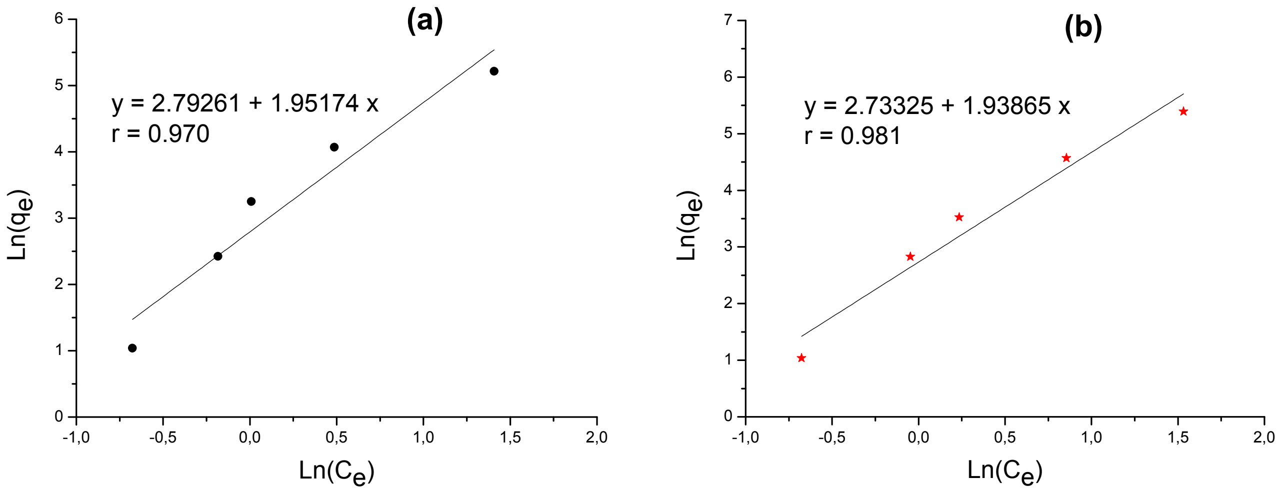

Figure 3. Linear form of Freundlich isotherm for the biosorption onto *Ceramium virgatum.*
(a) for Pb(II) biosorption ; (b) for Cd(II) biosorption
(Biomass concentration: 4 g.L-1 ; contact time: 60 min ; pH: 5.5 ; temperature: 20°C)

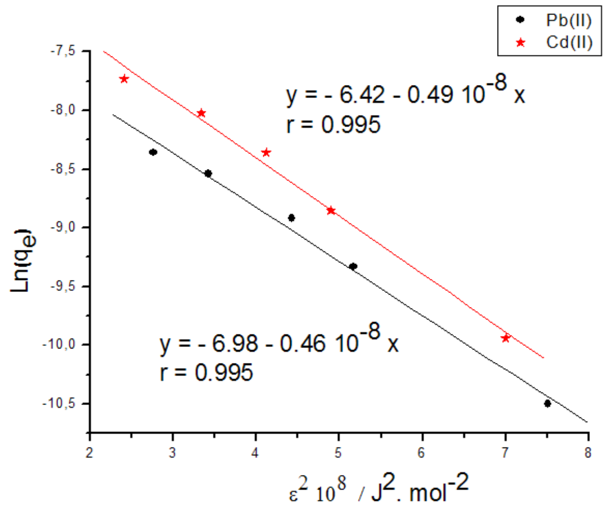

Figure 4. D-R isotherm plots for biosorption of Pb(II) and Cd(II) onto *Ceramium virgatum* alga.
(pH = 5.5 ; biomass concentration 4 g.L^{-1} ; contact time: 60 min ; temperature: 20 °C)

Ceramium virgatum biomass could take place by chemisorption mechanism as describe by Sarı *et al.* [14].

The kinetic study of biosorption of metal ions by alga was carried out by using pseudo-first order model [15] and pseudo second-order model [16]. The conformity between experimental data and the model predicted values was expressed by correlation coefficient (r). The pseudo-first order kinetic model proposed by Lagergren is generally expressed by its integral form as follows:

$$\mathrm{Ln}(q_e - q_t) = \mathrm{Ln}q_e - k_1 t \qquad (10)$$

where q_e and q_t (mg.g^{-1}) are the amount of the metal ions biosorbed at equilibrium and t(min), respectively, and k_1(min^{-1}) is the rate constant of the equation.

Results obtained by applying the first-order kinetic model to the experimental data were given in Table.2. Experimental data were also used by the pseudo-second order kinetic model which is given in the following form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \qquad (11)$$

Where k_2 (g. mg^{-1}.min^{-1}) is the rate constant of biosorption, qe and q_t (mg.g^{-1}) are the amount of metal ions biosorbed at equilibrium and t(min), respectively.

The values of k_1, q_e, k_2 were obtained from the slopes and intercepts of plots giving Ln(q_e-q_t) versus t and t/q_t versus t at different temperatures. The linear plots of t/q_t versus t for the pseudo-second order kinetic model for the biosorption of two metal ions onto alga biomass at 20-50 °C were shown in Figs. 5a and 5b, respectively.

The pseudo-first order and pseudo-second order parameters for the biosorption of Pb(II) and Cd(II) onto *Ceramium virgatum* biomass at different temperatures are given in Table II.

When the correlation coefficients of models were

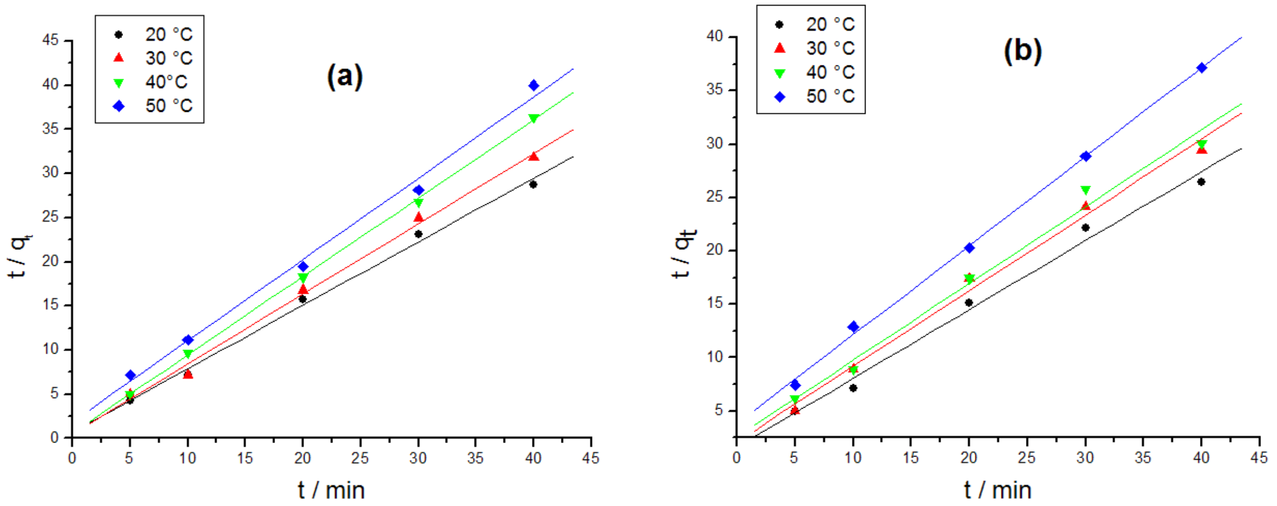

Figure 5. Pseudo-second order kinetic plots at different temperature.
(a) for Pb(II) biosorption ; (b) for Cd(II) biosorption
(*pH: 5.5, biomass concentration: 4g.L^{-1}, contact time: 60 min, initial concentration: 10 mg. L^{-1}*)

Table II. Pseudo-first order and pseudo-second order for the biosorption of Pb(II) and Cd(II) onto *Ceramium virgatum* biomass at different temperatures.

Temperature (°C)	$q_{e,exp}$ $(mg.g^{-1})$	Pseudo-first order			Pseudo-second order		
		k_1 (min^{-1})	$q_{e1,cal}$ $(mg.g^{-1})$	r	k_2 $(g.\ mg^{-1}.min^{-1})$	$q_{e2,cal}$ $(mg.g^{-1})$	r
Pb(II)							
20	1.42	$4.3\ 10^{-2}$	0.46	0.956	0.25	1.56	0.992
30	1.38	$4.0\ 10^{-2}$	0.44	0.806	0.23	1.41	0.992
40	1.34	$3.4\ 10^{-2}$	0.41	0.867	0.21	1.37	0.995
50	1.30	$3.1\ 10^{-2}$	0.40	0.973	0.19	1.20	0.999
Cd(II)							
20	1.40	$4.5\ 10^{-2}$	0.58	0.785	0.61	1.41	0.993
30	1.36	4.410^{-2}	0.53	0.888	0.57	1.28	0.998
40	1.32	2.410^{-2}	0.48	0.965	0.47	1.18	0.999
50	1.28	1.910^{-2}	0.44	0.893	0.43	1.09	0.992

compared, second order has a greater (r) value than that of first order. In addition, the theoretical values $q_{e2,cal}$ were closer to experimental $q_{e,exp}$ values. In the view of these results, it can be said that pseudo-second order kinetic model is the most compatible with the experimental data and describe better the kinetic process of biosorption of Pb(II) and Cd(II) by *Cermium virgatum.*

The thermodynamic parameters were calculated by the following equations:

$$LnK_D = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (12) \qquad (\text{Van't Hoff equation})$$

$$\Delta G^0 = -RTLnK_c \qquad (13)$$

Where $K_D = (q_e / C_e)$ is the adsorption equilibrium constant, T is absolute temperature (K), R is a universal gas constant. The plot giving LnK_D versus 1/T (Fig.6) allows to compute ΔH^0 and ΔS^0 values from the slope and the intercept of Van't Hoff equation. The calculated parameters are shown in Table III.

Table III. Thermodynamic parameters for Cd(II) and Pb(II) biosorption onto *Ceramium virgatum.*

T(K)	ΔG^0 $(kJ.\ mol^{-1})$	ΔH^0 $(kJ.\ moL^{-1})$	ΔS^0 $(kJ.\ mol^{-1}.\ K^{-1})$
Pb(II)			
293	-19.1	-26.5	-25.2
303	-18.9		
313	-18.7		
323	-18.3		
Cd(II)			
293	-18.4	-26.8	-28.6
303	-18.1		
313	-18.0		
323	-17.5		

The negative ΔG^0 values indicated feasible and spontaneous process of the biosorption. The decrease in ΔG^0 values with increase in temperature shows a decrease in feasibility of biosorption at higher temperatures. The negative ΔH^0 is indicator of exothermic nature of the biosorption and also its magnitude gives information on the type of biosorption, which can be either physical or chemical [17]. Therefore, the ΔH^0 values showed that the biosorption processes of Pb(II) and Cd(II) onto *Ceramium virgatum* biomass were taken place via chemisorption. The mean free energy values obtained by D-R model also confirm this result. The ΔS^0 parameter was found to be -25.2 kJ. $mol^{-1}.K^{-1}$ for Pb(II) biosorption and -28.6 kJ. $mol^{-1}.K^{-1}$ for Cd(II) biosorption. The negative ΔS^0 values suggest a

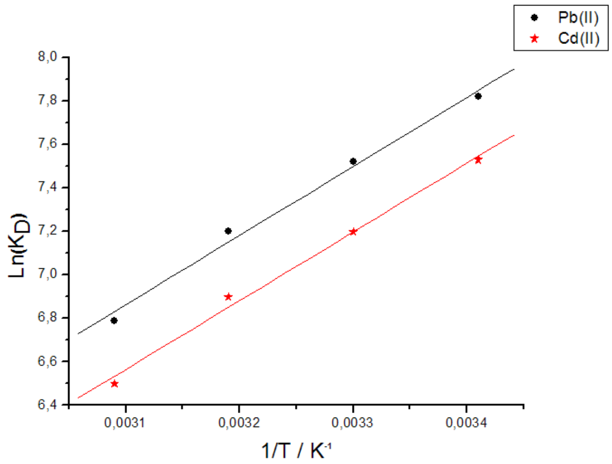

Figure 6. Plot of LnK_D versus 1/T for the estimation of thermodynamic parameters of biosorption of Pb(II) and Cd(II) into *Ceramium virgatum* alga.

decrease in the randomness at the solid/solution interface during the biosorption process [14,18,19]. Fourier Transform Infrared spectroscopy (FTIR) was used to analyze the functional groups in the fresh-dried algal biomass. Fig.7 shows the FTIR spectra of pristine and metal-loaded biomass sample. The peak at 3412 cm^{-1} was due to bounded hydroxyl (-OH) or amine (-NH) groups. This peak shifts to 3406 and 3417 cm^{-1} when Pb(II) and Cd(II) were loaded, respectively, showing the intervention of these groups to biosorption process. The peak at 2981 cm^{-1} can be assigned to the –CH group of unloaded biomass sample. This peak did not undergo any shifting when the metal ion is loaded; showing clearly that this group is not involved in biosorption process. The peak at 1729 cm^{-1} could be attributed to stretching vibration of carbonyl group (-CO) into carboxylic function. The peak observed at 1028 cm^{-1} was assigned to the (-CO) stretching to alcohols and carboxylic acids. The asymmetric stretching vibration at 3412 cm^{-1} was shifted to 3406 and 3417 cm^{-1} after biosorption of Pb(II) and Cd(II), respectively. These change in (-OH) peak indicate that hydroxyl group had been changed from multimer to monopolymer or even dissociative state [20] which showed that the degree of the hydroxyl polymerization in biomass was decreased by binding of Pb(II) and Cd(II). The carboxylic peak at 1729 cm^{-1} was observed at 1643 cm^{-1} for both Pb(II) and Cd(II)-loaded biomass. The peak of C-O group was shifted to 1025 cm^{-1} after Pb(II) sorption and 1013 cm^{-1} after Cd(II) sorption. These results indicated that the free carboxylic groups changed into carboxylate, which occurred during the reaction of the metal ions and carboxyl groups of the biosorbent. Moreover, the chemical process occurred when the metal ions in the solution was transferred to the biomass and chemical bonds were formed between the metal ions and the carboxyl ($-COO^-$), hydroxyl (-OH), and amine (-NH) groups of the biomass.

The adsorption capacity of *Cermium virgatum* biomass for removal of Pb(II) and Cd(II) have been compared with that of different adsorbents reported in literature and the value of adsorption

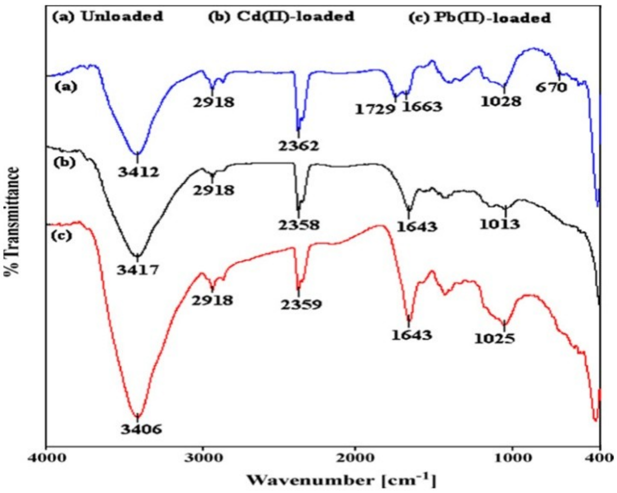

Figure 7. FTIR spectrum of pristine, Pb(II)-loaded and Cd(II)-loaded biomass algal.

Table IV. Comparison of adsorption capacity of *Ceramium virgatum* biomass for Pb(II) and Cd(II) with that of other adsorbents.

Adsorbents	Biosorption capacity ($mg.g^{-1}$)		Reference
	Pb(II)	Cd(II)	
Caulerpa racimosa	34.5	29	[21]
Calcite	19.92	18.52	[22]
Olive cake	19.53	10.56	[23]
Wheat bran	62	21	[24]
Cystine-modified biomass	45.9	11.6	[25]
Ceramium virgatum	-	39.7	[14]
Ceramium virgatum	53.9	51.6	Present study

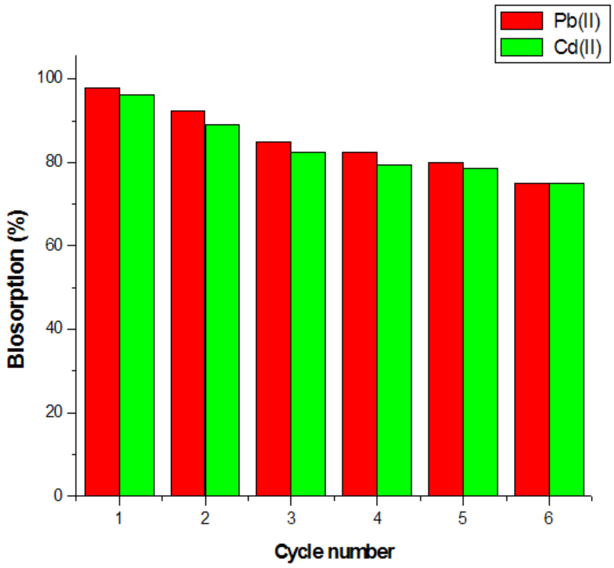

Figure 8. Reusability of *Ceramium virgatum* alga with repeated sorption-desorption cycle.
(pH = 5.5; biomass concentration: 4g. L^{-1}; initial concentration: 10 mg. L^{-1})

capacities have been presented in Table IV. These values are reported in the form of monolayer adsorption capacity. It can be noteworthy that the *Cermium virgatum* alga has an important potential for the removal of Pb(II) and Cd(II) ions from aqueous solutions.

The regeneration of the biosorbent is one of the key factors for assessing of its power to be easily sold and reused many times. This property offers an economic gain and protects in some way the environment.

Desorption agent 1M HNO_3 (10 mL) were used to recover the Pb(II) and Cd(II) ions from the algal biomass. The reusability of the biosorbent was tested during six consecutive biosorption-desorption cycles as it is presented by Figure 8. The lost in the biosorption capacity of the biomass after three sorption-desorption cycles and for the both metal ions was determined to be almost 8 %. After six cycles and for the both metal ions, this percentage of biosorption loss did not exceed 20 %. These results indicated that *Ceramium virgatum* alga offers a potential ability to be used repeatedly in Pb(II) and Cd(II) biosorption studies without a great loss in the biosorption capacity.

CONCLUSION

In this study, batch biosorption experiments for the removal of Pb(II) and Cd(II) from aqueous solutions have been carried out using algal biomass (*Cermium virgatum*). The biosorption characteristics have been examined at different pH values, contact time, adsorbent dosage and temperature. The Langmuir adsorption isotherm model was better fitted to represent the experimental data. The monolayer adsorption capacity of *Ceramium vergatum* biomass for Pb(II) and Cd(II) ions was obtained to be 53.9 mg.g^{-1} and 51.6 mg.g^{-1}, respectively. From the D-R isotherm model, the mean free energy was calculated as 10.3 kJ. mol^{-1} for Pb(II) biosorption and 10.1 kJ. mol^{-1} for Cd(II) biosorption, indicating that the biosorption of both metal ions was taken place by chemical process. Experimental data obtained from kinetic rates were better described by pseudo-second order model than pseudo-first order model as evident from correlation coefficients values. The calculated thermodynamics parameters (ΔG^0, ΔH^0 and ΔS^0) showed that the biosorption of Pb(II) and Cd(II) ions onto *Ceramium virgatum* biomass is feasible, spontaneous and exothermic in nature. Analysis by infrared spectroscopy (FTIR) proved that the carboxylic ($-COO^-$), hydroxyl (-OH), and amine (-NH) groups are responsible for the binding of the metal ions. The reusability of the biosorbent was good after six consecutive sorption-desorption cycles and reached a high reuse yield (90 %) after three regeneration cycles. This work illustrated an alternative solution for the management of the unwanted biological materials, such as *Ceramium virgatum*, which is considered as one of the fast-growing marine algae. It could be, to some extent, utilized as a biosorbent for the removal of heavy metals from the low strength wastewater.

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