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Removal of Lead and Cadmium Ions From Aqueous Solutions Using Dried Marine Green Macroalga (*Caulerpa racemosa)*

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ABSTRACT: In this study *Caulerpa racemosa* has been characterized and used for the removal of Cd(II) and Pb (II) from aqueous solutions. The effect of pH, adsorbent dosage, contact time and temperature on adsorption process was studied in batch experiments. Langmuir and Freundlich models were applied to describe the biosorption isotherm of the metal ions by *C. racemosa* biomass. The adsorption data can be well described by Langmuir isotherm. The monolayer biosorption capacity of C. *racemosa* biomass for Pb(II) and Cd(II) ions was found to be 34.5 mg/g and 29 mg/g, respectively. Kinetics data of both metal ions were best described by pseudo second order model.The thermodynamic studies indicated that the adsorption was spontaneous and exothermic in nature. The analysis with FTIR indicated that possible functional groups involved in metal sorption by this alga were O–H bending, N–H stretching, C–N stretching, C–O and S=O stretching.

Key words:*Caulerpa racemosa,* Langmuir and Freundlich models, Biosorption, FTIR analysis, Kinetic

INTRODUCTION

Among various organic and inorganic pollutants, heavy metal ions are very toxic and carcinogenic in nature. The presence of heavy metals in the aquatic environment has been of great concern because of their toxicity at lower concentrations (Uba *et al.,* 2009; Aljuboury, 2009; Nasrabadi *et al.,* 2010).

Some metal ions are cumulative poisons capable of being assimilated and stored in the tissues of organisms, causing noticeable adverse physiological effects. Lead and Cadmium, are very toxic metal ions, as they are carcinogenic in nature (Moore & Ramamoorthy 1984). Cadmium, which is widely used and extremely toxic in relatively low dosages, is one of the principle heavy metals responsible for causing kidney damage, renal disorder, high blood pressure, bone fraction and destruction of red blood cells (Drash 1993). Because of the toxicity and bioaccumulation, Cd is considered as a priority pollutant by the U S Environmental Protection Agency. The permissible limit for Cd as described by WHO is 0.01 mg/dm^3. The main anthropogenic pathway through which Cd enters the water bodies is via wastes from industrial processes such as electroplating, plastic manufacturing, metallurgical processes and industries of pigments and Cd/Ni batteries (Cheremisinoff 1995).Lead is the most significant toxin of the heavy metals and its effects are of toxicological and neurotoxical natures which include irreversible brain damage. Inorganic forms of lead typically affect the central nervous system, peripheral nervous system, and hematopoietic, renal, gastrointestinal, cardiovascular, and reproductive systems. Organic lead toxicity tends to predominant affect the central nervous system. The other hazardous effects of lead are visual disturbances, convulsions, loss of cognitive abilities, antisocial behaviours, constipation, anaemia, tenderness, nausea, vomiting, severe abdominal pain, anaemia, and gradual paralysis in the muscles. Therefore, the removal of these toxic metal ions from water prior to supplying water for drinking, bathing, etc. is very important and urgent.

Numerous processes such as ion exchange, precipitation, phyto-extraction, ultra-filtration, reverse osmosis and electrodialysis have been used for the removal of heavy metal ions from aqueous solution (Yu & Kaewsarn 1999). However, technical or economic factors limit sometimes the feasibility of such processes. Biosorption as a wastewater treatment process has been found to be an economically feasible

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*Corresponding author E-mail: Yasser_102@yahoo.fr alternative for metal removal. Basically, it can be based on the following mechanisms: physical adsorption, ion exchange, complexation and precipitation. Biosorption may not necessarily consist of a single mechanism. In many sorption processes, several mechanisms often act in combination and it is difficult to distinguish between the single steps (Lacher & Smith 2002). Among the different biological substrates studied, algal biomass has received much attention due to the cost saving, low sensitivity to environmental and impurity factors, the possible contaminant recovery from the biomaterial and its elevated adsorption capacity, higher than activated carbon and comparable to those of synthetic ion exchange resins. *C. racemosa var. cylindracea* is one of the well-known invasive marine alga in Mediterranean Sea. Its dangerous invasion has been continuing on since 1991 and about eleven Mediterranean countries are threatened by this species. So far, there is no valid eradication method, for this species in the literature. Turning excess C. *racemosa* into biosorbents could be available answer to this problem (Cengiz & Cavas 2008).

The objective of the present work was to assess the potential of *Caulerpa racemosa* var. *cylindracea*, for the biosorption of lead and cadmium from aqueous solution. The effects of pH values, contact time, adsorbent dosages and temperature, were studied. During the work program, pristine and metal-loaded algal biomasses were tested with Fourier transform infrared spectrometer (FTIR) to evaluate the functional groups that might involve in the sorption of both metal ions. These results would contribute to a better understanding of the biosorption phenomena and aid in the development of potential biosorbents using locally derived sorbents, which possess high capacities for heavy metal uptake from aqueous solutions.

MATERIALS & METHODS

The raw biomass of *Caulerpa racemosa* was harvested from the coasts in Monastir, Tunisia.

The simples were washed with copious quantities of deionized 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 h. The dried algae biomass was chopped, sieved and the particles with an average of 0.5mm 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 (Ireland)).

The necessary amount of biomass was taken in a 100 mL stopper conical flask containing 25 mL of desired concentration of the test solution at the desired pH value. pH of the solution was monitored in a 5500 EUTECH pH Meter using FET solid electrode calibrated with standard buffer solutions by adding 0.1 mol/L HNO_3 and 0.1 mol/L NaOH solutions as per required pH value. Necessary amount of biomass was then added and contents in the flask were shaken for the desired contact time in an electrically thermostated reciprocating shaker at 100 rpm. The experiments were repeated at 20, 30 and 40 C°. The time required for reaching the equilibrium condition estimated by drawing samples at regular intervals of time till equilibrium was reached. The contents of the flask were filtered through filter paper and the filtrate was analyzed for remaining metal concentration in the sample using Atomic Absorption Spectrophotometer (VARIAN SPETRA AA 55, USA). The percent biosorption of metal ion was calculated as follows:

$$Biosorption(\%) = \frac{\left(C_i - C_f\right)}{C_i} \times 100 \qquad (1)$$

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

All the investigations were carried out in triplicate to avoid any discrepancy in experimental results with the reproducibility and the relative deviation of the order of ±0.5% and ±2.5%, respectively.

The effect of pH on biosorption was conducted by using a solution having 10 mg/L of Pb(II) and 10 mg/L of Cd(II) concentration with a biomass dosage of 20 g/L.

Throughout the study, the contact time was varied from 5 to 120 min, the pH from 2 to 8, the initial metal concentration from 10 to 400 mg/L, and the biosorbent dosage from 2 to 40 g/L.

FT-IR spectroscopy was used to detect vibration frequency changes in the algal sorbent. The spectra were collected by an FTS-135 (Bio-Rad) spectrometer within the range 400–4000cm^{-1} using a KBr window. The background obtained from the scan of pure KBr was automatically subtracted from the sample spectra.

RESULTS & DISCUSSION

Various authors have observed that solution pH is an important parameter affecting heavy metal biosorption by seaweed species (Figueira & Mathieu 1999, Matheickal & Woodburn 1999). The surface groups of seaweed species e.g. carboxyl and sulphonate display weakly acidic characteristics. Therefore, the optimum pH for metal uptake is related to the pKa of these functionalities. However, the solution chemistry of the metal complexes involved must also be considered, as the speciation of metals in solution is pH dependant.

The effect of pH on the biosorption of Pb(II) and Cd(II) ions onto *Caulerpa racemosa* biomass was studied by changing pH values in the range, 2–8 and the results were presented in Fig. 1. The maximum biosorption was found to be 97% for Pb(II) and 91% for Cd(II) ions at pH 5. Therefore, all the biosorption experiments were adjusted at pH 5. At higher pH values, the biosorption yield for Cd(II) was dramatically decreased.

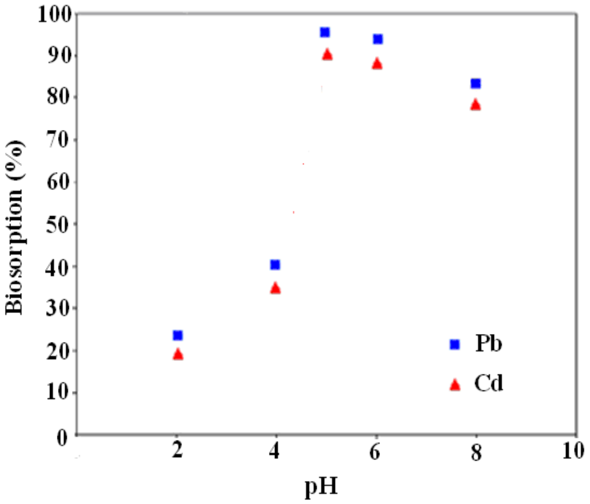

Fig. 1. Effect of pH on biosorption of Pb(II) and Cd(II) onto C. racemosa (metal concentration:10 mg/L; temperature: 20 °C)

At pH range, 2–4, the biosorption yield was in the range of 18–40% for both Pb(II) and Cd(II) ions. Increased positive charge (protons) density on the sites of biomass surface at low pH values (pH 2–4) restricted the approach of metal cations as a result of repulsive force. In contrast, when the pH value increased, biomass surface was more negatively charged and the biosorption of the metal ions with positive charge (Pb^{2+} and Cd^{2+}) was reached maximum around pH 5. Decrease in biosorption at higher pH (pH > 5) is due to the formation of soluble hydroxilated complexes of the metal ions and their competition with the active sites, and as a consequence, the retention would decrease.

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 (Mehta & Gaur 2005). It has been suggested that electrostatic 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 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 lower specific metal uptake, that is, a smaller amount of metal uptake per biomass unit.

The effect of biomass dosage on the biosorption of Pb(II) and Cd(II) ions was studied using different biomass dosage in the range, 2–40 g/L (Fig. 2). Results showed that the biosorption efficiency is highly dependent on the increase in biomass dosage of the solution. The maximum biosorption of the metal ions was attained at about biomass dosage, 20 mg/L and it was almost same at higher dosages.

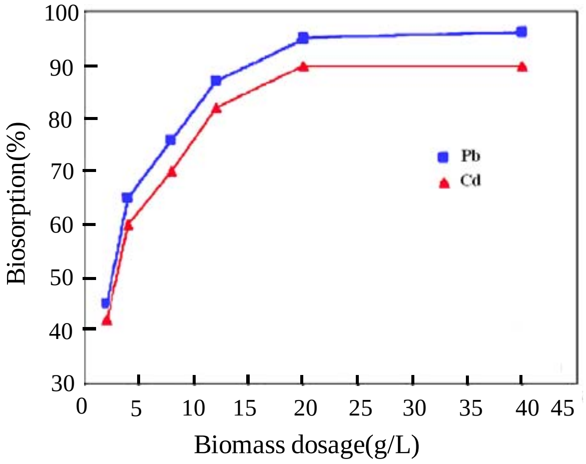

Fig. 2. Effect of biomass dosage on biosorption of Pb (II) and Cd(II) onto C. racemosa (metal concentration: 10 mg/L; pH: 5; temperature: 20 °C)

This trend could be explained as a consequence of a partial aggregation of biomass at higher biomass concentration, which results in a decrease in effective surface area for the biosorption. Therefore, the optimum biomass dosage was selected as 20 g/L for further experiments Previous work showed that the sorption of heavy metal ions by algae followed a two-step mechanism where the metal ion was physically/ chemically uptaken onto the surface of the algae before being taken up biologically into the cell (Volesky 1990). 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 to complete. In this case, since the alga was dried and 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.

Figs. 3a and 3b show the biosorption efficiency of Pb(II) and Cd(II) ions by *C. racemosa* as a function of contact time and temperature. As can be seen from Figs.3a and 3b, the biosorption efficiency increases with rise in contact time up to 60 min at 20–40 °C and after then it is almost constant. Therefore, the optimum contact time was selected as 60 min for further experiments. On the other hand, the biosorption yield decreased from 96 to 71 % for Pb (II) ion and from 91 to 68% for Cd (II) ion with increasing temperature from 20 to 40 °C during a 60 min-contact time. This result indicated the exothermic nature of Pb(II) and Cd(II) biosorption onto *C. racemosa* biomass.

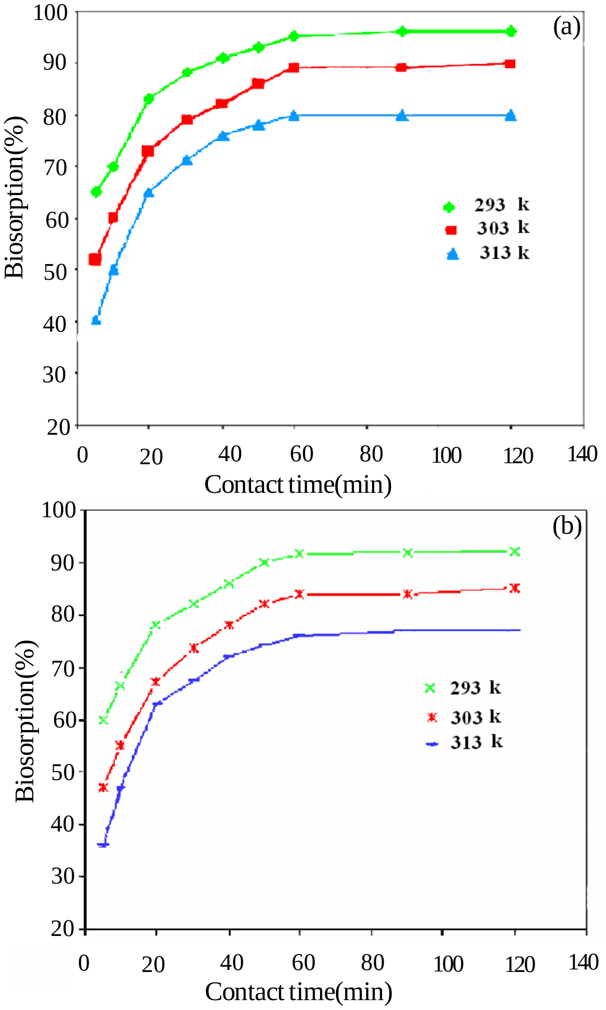

Fig. 3. Effect of contact time and temperature on biosorption onto C. racemosa (metal concentration: 10 mg/L; biomass dosage: 20 g/L; pH: 5). a) Pb(II), b) Cd (II)

To find out the mechanistic parameters associated with lead and cadmium adsorption, the results obtained by the adsorption experiments were analyzed by Langmuir and Freundlich models.The theoretical Langmuir adsorption isotherm model is best known to all the isotherm models, and describes the adsorption of a solute from a liquid solution. Langmuir adsorption isotherm applied to equilibrium adsorption assuming mono-layer adsorption onto a surface with a finite number of identical sites and is represented as follows:

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

where q_e is the equilibrium metal ion concentration on the biosorbent (mg/g), C_e is the equilibrium metal ion concentration in the solution (mg/L), q_{max} is the monolayer biosorption capacity of the biosorbent (mg/g), and b is the Langmuir biosorption constant (L/mg) relating the free energy of biosorption .

Linear plots of C_e/q_e vs C_e (Fig. 4) were employed to determine the value of q_{max} (mg/g) and b (L/mg). The data obtained with the correlation coefficients (r^2) were listed in Table 1.

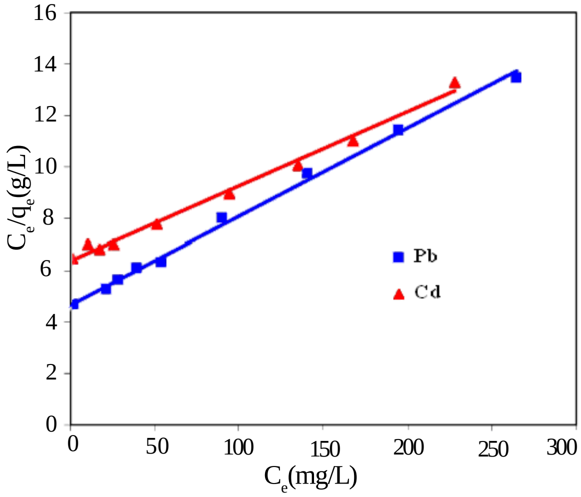

Fig. 4. Langmuir isotherm plots for biosorption of Pb(II) and Cd(II) onto C. racemosa (biomass dosage: 20 g/L; contact time: 60 min; pH: 5; temperature :20°C)

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

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \qquad (3)$$

The Freundlich isotherm constant n is an empirical parameter that varies with the degree of heterogeneity and K_f is related to adsorption capacity. The amount of absorbent required to reduce any initial concentration to predetermined final concentration can be calculated (Fig.5).

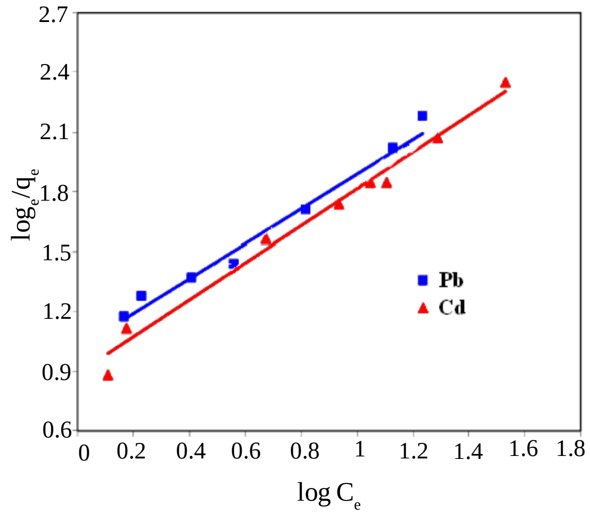

Fig. 5. Freundlich isotherm plots for biosorption of Pb(II) and Cd(II) C. racemosa (biomass dosage: 20 g/L; contact time: 60 min; pH: 5; temperature: 20°C)

Table1. Adsorption isotherm parameters for Cd (II) and Pb (II) biosorption onto C. racemosa

Metals	Langmuir constants			Freundlich constants		
	$q_{max\ (mg/g)}$	b $_{(L/mg)}$	r^2	k_f	1/n	r^2
Cd (II)	29	$7.1x10^{-2}$	0.996	7.81	0.9	0.980
Pb (II)	34.5	$5.2x10^{-2}$	0.991	10.51	0.9	0.978

Table 1 shows that the experimental data are better fitted to Langmuir (r^2 = 0.991 and 0.996 for Pb(II) and Cd(II) , respectively) than Freundlich (r^2 = 0.978 and 0.98 for Pb(II) and Cd(II) , respectively) adsorption isotherm The study of adsorption kinetics describes the solute uptake rate and evidently these rate controls the residence time of adsorbate uptake at the solid–solution interface including the diffusion process. The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbent as well as on the mass transfer process (Metcalf 2003). The results obtained from the experiments were used to study the kinetics of metal ion adsorption.

The rate kinetics of metal ion adsorption on *C. racemosa* biomass was analyzed using pseudo-first order and pseudo-second order (Ho & Foster 2000).

The conformity between experimental data and the model predicted values was expressed by correlation coefficients (r^2).

The integral form of pseudo-first order kinetic model is generally expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (4)$$

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

Results obtained by applying the first-order Lagergren model to the experimental data were given in Table 2

Experimental data were also tested by the pseudo-second order kinetic model which is given in the following form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{t}{q_2} \qquad (5)$$

where k_2 (gmg^{-1} min^{-1}) is the rate constant of adsorption, q_2 is maximum adsorption capacity (mg/g) (. Ho & McKay 1999). The values of k_1, q_e and k_2, q_2 were obtained from the slopes and intercepts of plots of log (qe - q_t) versus t and t/qt versus t at different temperatures. The linear plots of t/qt versus t for the pseudo-second order model for the biosorption of Pb(II) and Cd(II) ions onto the alga biomass at 20–40°C were shown in Fig. 6.

The Pseudo-first-order and pseudo-second-order parameters for the biosorption of Pb(II) and Cd(II) onto *C. racemosa* biomass at different temperatures were given in Table 2.

When the correlation coefficients of models were compared, second order equation has a greater r^2 values. Then, it is inferred that second order equation is better described than the pseudo first -order kinetic model.

Thermodynamic parameters such as Gibbs free energy change ΔG^0 , standard enthalpy change ΔH^0 and standard entropy change ΔS^0 were also found out to give more information about the nature of sorption process (Bursali &Yurdakoc 2009). The thermodynamic parameters were calculated by the following equations:

$$\ln k_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (6) \quad \text{(Van't Hoff equation)}$$

$$\Delta G^\circ = -RT \ln k_c \qquad (7)$$

where $K_c = (q_e / Ce)$ is the adsorption equilibrium constant, T is absolute temperature (K), R is gas constant. When ln Kc versus $1/T$ is plotted (Fig.7), ΔH^0 and ΔS^0 values can be computed from slope and intercept of the van't Hoff equation. The calculated parameters were given in Table 3.

The negative ΔG^0 values indicated thermodynamically feasible and spontaneous nature of the biosorption. The decrease in ΔG^0 value 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

Table 2. Pseudo-first-order and pseudo-second-order parameters for the biosorption of Pb (II) and Cd (II) onto C. racemosa at different temperatures

	Pseudo-first-order			Pseudo-second-order		
Temperature	k_1(1/min)	q_e(mg/g)	R^2	k_2 (g/mg.min)	q_e(mg/g)	R^2
Pb (II)						
20	$8.4\ 10^{-2}$	0.56	0.977	0.29	1.01	0.990
30	$7.5\ 10^{-2}$	0.54	0.974	0.24	0.98	0.998
40	$7.3\ 10^{-2}$	0.44	0.982	0.22	0.88	0.990
Cd (II)						
20	$8.4\ 10^{-2}$	0.63	0.970	0.25	0.99	0.999
30	$8\ 10^{-2}$	0.53	0.972	0.19	0.95	0.999
40	$7.3\ 10^{-2}$	0.44	0.971	0.17	0.9	0.998

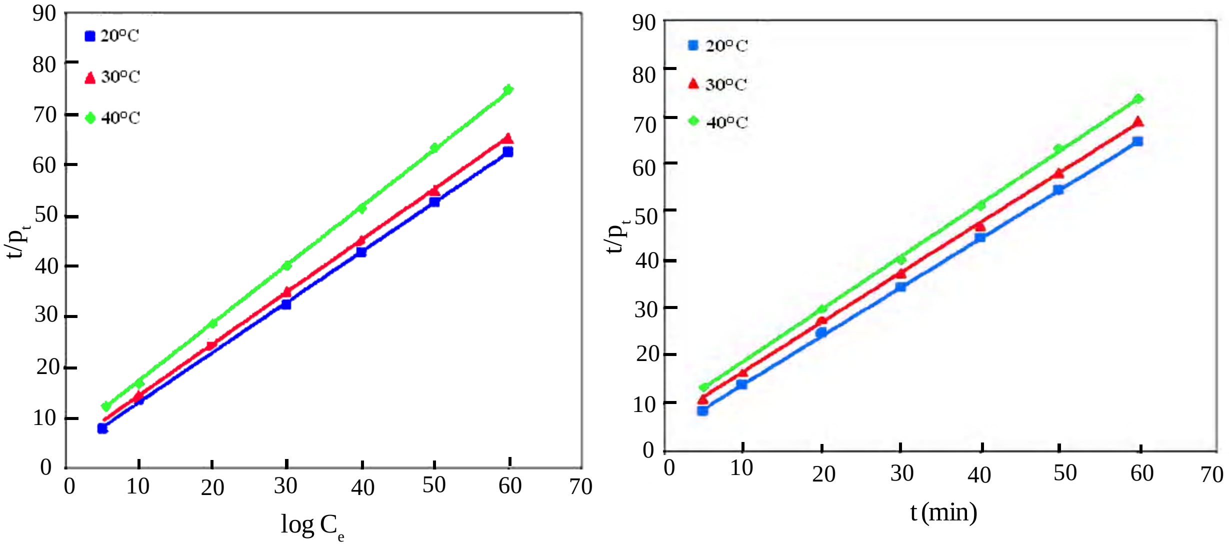

Fig. 6. Pseudo-second-order kinetic plots at different temperatures: (a) for Pb(II) biosorption (b) for Cd(II) biosorption

Table 3.Thermodynamic parameters for Cd (II) and Pb (II) biosorption onto C. racemosa

T(k)	ΔG^0 (kJmol^{-1})	ΔH^0 (kJmol^{-1})	ΔS^0 (Jmol^{-1}k^{-1})
Cd (II)			
298	-16.3	-32.8	-55.8
308	-16		
318	-15.2		
Pb (II)			
298	-16.7	-30.1	-45.7
308	-16.4		
318	-15.6		

Table 4. Pristine wave number (cm^{-1}) of dominant peak obtained from transmission spectra

	Pristine	Cd^{2+} loaded	Pb^{2+} loaded
Carboxylic acid			
O-H Stretching	2930	2932	2930
C=O Stretching	-	-	-
C-O Stretching	1248	1246	1246
O-H Bending	1420	-	-
Amine			
N-H Stretching	3410	3396	3415
N-H Bending	1657	1655	1655
C-N Stretching	1330	-	-
Amide			
N-H Stretching	3410	3396	3415 3340
C-O Stretching	1657	1655	1655
Amino			
C-O	1548	1540	1540
N-H bending	1550	1542	1542
Sulfonyl			
S=O Stretching	-	1389	1389
Sulfonate			
S=O Stretching	1370	-	-
S-O Stretching	915	915	915

either physical or chemical. Therefore, the ΔH^0 values showed that the biosorption processes of Pb(II) and Cd(II) ions onto *C. racemosa* biomass were taken place via chemisorption.The ΔS^0 parameter was found to be -45.7 J/mol K for Pb(II) biosorption and -55.8 J/mol K for Cd (II) biosorption. The negative ΔS^0 value suggests a decrease in the randomness at the solid/ solution interface during the biosorption process.

The functional group is one of the keys to understand the mechanism of metal binding on the algal surface. FT-IR was used to analyze the functional groups in the fresh-dried algal biomass. The results of FT-IR transmission spectra are shown in Table 4. There were several functional groups found in the structure of C. *racemosa* such as carboxylic acid, amine, amide, amino, sulfonyl, and sulfonate groups. In comparing between pristine and metal loaded algal biomass, it was observed that there was a shift (more than 14 cm^{-1}) in wave number of dominant peaks associated with the loaded metal. This shift in the wavelength showed that there was a metal binding process taking place on the surface of the alga (Matheickal 1998). The carboxylic group contained the following minor groups: O–H stretching, O–H bending, and C–O stretching. The O–H bending group was observed to shift clearly at a wave number of 1420 $cm^{-1}$for two heavy metals while the other groups did not seem to have shifts of the wave number of the peak. These indicated that there was a high potential that O–H bending groups from carboxylic acid involved with heavy metals binding.

For amine group, there were changes in wave number for N–H stretching in the Cd^{2+} sorptions. The C–N stretching was found to disappear with the sorptions of Cd^{2+} and Pb^{2+}. The N–H bending group did not seem to change for both metals. These could be interpreted that N–H stretching in amine group was associated with Cd^{2+} sorption, and C–N stretching was for both metal sorption. On the other hand, N–H bending was thought not to involve in the metal binding by this biomass.

The observation for amide group revealed that N–H stretching was slightly shifted by Cd^{2+} sorption from 3410 to 3396 cm^{-1}. N–H stretching was also affected by the sorption of Pb^{2+} where the new peak occurred at a wave number of 3340 cm^{-1}. For this case, the new peak occurred while the old peak still existed. This could imply that this N–H stretching was available in excess quantity for the sorption of Pb^{2+}. The C–O stretching group in this amide group did not show shift in wavelength, which suggested that this was not involved with the sorption. In contrast, C–O in amino group seemed to play an important role for all metal sorption as a shift in the wavelength was always found. The N–H bending in this amino group, however, was not found to involve with the sorption of Cd^{2+}, and Pb^{2+}. The S=O stretching in the sulfonyl and sulfonate groups was involved with two metal sorptions since there was a shift in sulfonate peak at 1370 $cm^{-1}$to sulfonyl at 1389 cm^{-1}. S–O stretching was not associated with the sorption of Cd^{2+}, and Pb^{2+}.

CONCLUSION

In this study, batch adsorption experiments for the removal of Cd(II) and Pb (II) from aqueous solutions have been carried out using algal biomass*(Caulerpa racemosa)*.The adsorption characteristics have been examined at different pH values, contact time, adsorbent dosages and temperature. The Langmuir adsorption isotherm models were better fitted to represent the experimental data. The monolayer adsorption capacity of *C. racemosa* biomass for Pb(II) and Cd(II) was obtained to be 34.5 and 29 mg/g ions, respectively. Experimental data obtained from rate kinetics were better described by pseudo-second order model than pseudo-first order model as evident from correlation co-efficient values *(r^2)*. The calculated thermodynamic parameters (ΔG^0 , ΔH^0 and ΔS^0) showed that the biosorption of Pb(II) and Cd(II) ions onto *C. racemosa* biomass was feasible, spontaneous and exothermic under examined conditions.

It was proven that the possible functional groups in this alga responsible for the metals binding were O–H bending, N–H stretching, C–N stretching, C–O and S=O stretching. This work illustrated an alternative solution for the management of the unwanted biological materials where *C. racemosa*, one of the fast-growing marine algae, could be, to some extent, utilized as a biosorbent for the removal of heavy metals from the low strength wastewater.

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