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## Removal of lead and cadmium ions from aqueous solutions using the macroalga *Caulerpa racemosa*

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In this study, *Caulerpa racemosa* was characterised 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 the 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 the Langmuir isotherm. The monolayer biosorption capacity of *C. racemosa* biomass for Pb(II) and Cd(II) ions was found to be 34.5 and 29 mg · g<sup>-1</sup>, respectively. The mean free energy calculated from the Dubinin–Radushkevich isotherm indicated that the biosorption of Pb(II) and Cd(II) onto *C. racemosa* macroalga took place by chemisorption. Kinetics data of both metal ions were best described by a pseudo-second-order model. Thermodynamic studies showed that the adsorption was spontaneous and exothermic in nature. 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.

**Keywords:** *Caulerpa racemosa*; Langmuir and Freundlich models; biosorption; FTIR analysis; kinetic; heavy metal biosorption; Dubinin–Radushkevich isotherm

### 1. 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.

Some metal ions are cumulative poisons capable of being assimilated and stored in the tissues of organisms, causing noticeable adverse physiological effects. Lead (Pb) and cadmium (Cd) are very toxic metal ions because they are carcinogenic in nature [1]. Cd(II), 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 fractures and the destruction of red blood cells [2]. Because of its toxicity and bioaccumulation, Cd is considered as a

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priority pollutant by the US Environmental Protection Agency. The permissible limit for Cd(II), as described by the World Health Organization (WHO) is  $0.01 \text{ mg} \cdot \text{dm}^{-3}$ . The main anthropogenic pathway through which Cd(II) enters water bodies is via wastes from industrial processes such as electroplating, plastic manufacture, metallurgical processes, pigment industries and Cd/Ni batteries [3]. Pb(II) is the most significant heavy metal toxin and its effects are of a toxicological and neurotoxic nature and include irreversible brain damage. Inorganic forms of lead typically affect the central nervous system, peripheral nervous system and haematopoietic, renal, gastrointestinal, cardiovascular and reproductive systems. Organic lead toxicity tends to predominantly affect the central nervous system. Other hazardous effects of lead are visual disturbances, convulsions, loss of cognitive abilities, antisocial behaviours, constipation, anaemia, tenderness, nausea, vomiting, severe abdominal pain, and gradual paralysis of the muscles [1,4]. Therefore, the removal of these toxic metal ions from water prior to its supply for drinking, bathing, etc. is very important and urgent.

Numerous processes such as ion exchange, precipitation, phytoextraction, ultrafiltration, reverse osmosis and electrodialysis have been used to remove heavy metal ions from aqueous solution [5]. However, technical or economic factors sometimes limit the feasibility of such processes. Biosorption as a wastewater treatment process has been found to be an economically feasible alternative for metal removal. Basically, it may 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 [6]. Among the different biological substrates studied, algal biomass has received much attention due to the cost savings, low sensitivity to environmental and impurity factors, possible contaminant recovery from the biomaterial and its elevated adsorption capacity, which is higher than activated carbon and comparable with synthetic ion-exchange resins. *C. racemosa* var. *cylindracea* is a well-known invasive marine alga in the Mediterranean Sea. Its dangerous invasion has continued since 1991 and ~ 13 Mediterranean countries are threatened by this species. To date, there is no valid eradication method for this species in the literature. Turning excess *C. racemosa* into biosorbents might be one answer to this problem [7].

The objective of this study was to assess the potential of *C. racemosa* var. *cylindracea*, for the biosorption of lead and cadmium from aqueous solution. The effects of pH, contact time, adsorbent dosages and temperature were studied. During the study, raw and metal-loaded algal biomasses were tested with a Fourier transform infrared (FTIR) spectrometer to evaluate the functional groups that might be involved 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.

## 2. Materials and methods

### 2.1. Materials

The raw biomass of *C. racemosa* was harvested from the coast at Monastir, Tunisia. Samples were washed with copious quantities of deionised water to remove extraneous materials and to release common ions (e.g.  $\text{Na}^+$  and  $\text{Ca}^{2+}$ ) present in seawater. The washed biomass was dried at  $60^\circ\text{C}$  for 48 h. The dried algae biomass was chopped, sieved and particles with an average size of 0.5 mm were used for biosorption experiments. Stock metal solutions at various concentrations were prepared by dissolving analytical reagent grade lead nitrate and cadmium nitrate (Sigma-Aldrich, Ireland).

## 2.2. Batch biosorption experiments

The necessary amount of biomass was taken in a 100 mL stopper conical flask containing 25 mL of the desired concentration of the test solution at the desired pH. The pH of the solution was monitored in a 5500 EUTECH pH meter using a FET solid electrode calibrated with standard buffer solutions by adding  $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ HNO}_3$  and  $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ NaOH}$  solutions as per required pH value. The necessary amount of biomass was then added and the flask contents were shaken for the desired contact time in an electrically thermostated reciprocating shaker at 100 rpm. The experiments were repeated at 20, 30 and  $40^\circ\text{C}$ . The time required to reach equilibrium was estimated by drawing samples at regular intervals until equilibrium was reached. The flask contents were filtered through filter paper and the filtrate was analysed for the remaining metal concentration in the sample using an atomic absorption spectrophotometer (VARIAN SPETRA AA 55, USA). The per cent biosorption of metal ion was calculated as follows:

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

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

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

The effect of pH on biosorption was conducted by using a solution with  $10 \text{ mg} \cdot \text{L}^{-1} \text{ Pb(II)}$  and  $10 \text{ mg} \cdot \text{L}^{-1} \text{ Cd(II)}$  with a biomass dosage of  $20 \text{ g} \cdot \text{L}^{-1}$ .

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  $400 \text{ mg} \cdot \text{L}^{-1}$  and the biosorbent dosage from 2 to  $40 \text{ g} \cdot \text{L}^{-1}$ .

## 2.3. FTIR spectroscopy

FTIR 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  $400\text{--}4000 \text{ cm}^{-1}$  using a KBr window. The background obtained from the scan of pure KBr was automatically subtracted from the sample spectra.

## 3. Results and discussion

### 3.1. Effect of pH solution

The biosorption capacity of the alga strongly depends on the pH of the equilibrium solution, so characterisation of its effect on adsorption studies is necessary for an accurate evaluation of equilibrium parameters. Therefore, if the metal binding groups are weakly acidic or basic, the availability of free sites is dependent on the pH. The biosorption of Pb(II) and Cd(II) was studied over a pH range of 2–8 and the results are given in Figure 1.

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 to pH 5. At higher pH values, the biosorption yield for Cd(II) was dramatically decreased.

Within the pH range 2–4, the biosorption yield was in the range 18–40% for both Pb(II) and Cd(II) ions. Increased positive charge (protons) density on the biomass surface at low pH (2–4) restricted the approach of metal cations due to a repulsive force. By contrast, when the pH increased, the biomass surface was more negatively charged and the biosorption of metal ions with positive charge ( $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ ) reached a maximum at around pH 5. The decrease in biosorption

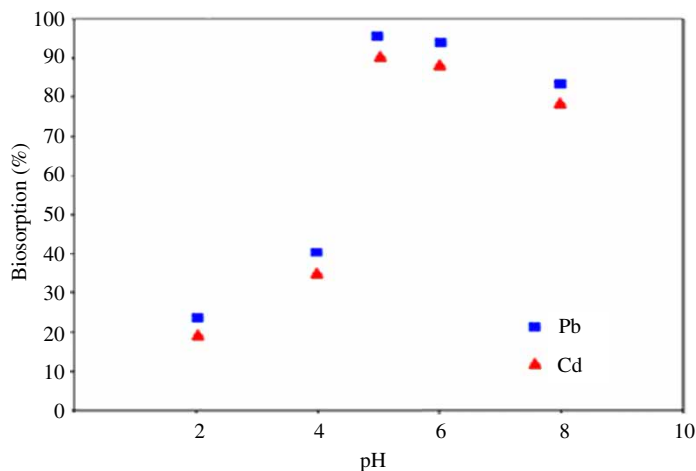


Figure 1. Effect of pH on biosorption of Pb(II) and Cd(II) onto *C. racemosa* (metal concentration,  $10 \text{ mg} \cdot \text{L}^{-1}$ ; temperature,  $20^\circ \text{C}$ ).

at higher pH ( $>5$ ) is due to the formation of soluble hydroxylated complexes of the metal ions and their competition with the active sites, as a consequence, retention decreases.

### 3.2. Effect of biosorbent concentration

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 [8]. It has been suggested that electrostatic interactions between cells may 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 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 is a lower specific metal uptake, i.e. 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 dosages in the range  $2\text{--}40 \text{ g} \cdot \text{L}^{-1}$  (Figure 2). The results showed that biosorption efficiency is highly dependent on the increase in biomass dosage of the solution. Maximum biosorption of the metal ions was attained at a biomass dosage of  $\sim 20 \text{ mg} \cdot \text{L}^{-1}$  and was almost same at higher dosages.

This trend could be explained by partial aggregation of biomass at higher biomass concentrations, which results in a decrease in the effective surface area for biosorption. Therefore, the optimum biomass dosage was selected as  $20 \text{ g} \cdot \text{L}^{-1}$  for further experiments.

### 3.3. Effects of contact time and temperature

Previous study has shown that the sorption of heavy metal ions by algae followed a two-step mechanism in which the metal ion was physically/chemically uptaken onto the surface of the algae before being taken up biologically into the cell [4]. The first step, known as passive transport, takes place quite rapidly, i.e. within 20–30 min, whereas the second biological step, or active transport, might take much longer to complete. In this case, because the alga was dried and biological functions were no longer active, sorption could only take place on the surface of the

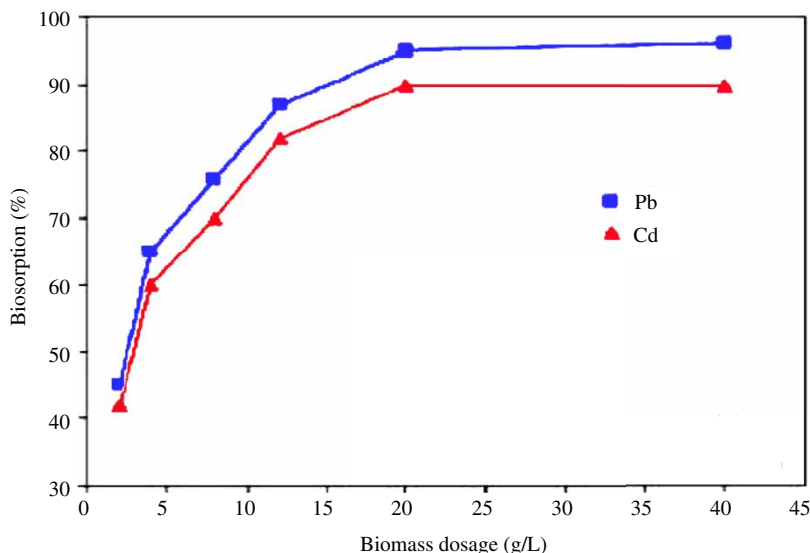


Figure 2. Effect of biomass dosage on biosorption of Pb(II) and Cd(II) onto *C. racemosa* (metal concentration,  $10 \text{ mg} \cdot \text{L}^{-1}$ ; pH 5; temperature,  $20^\circ\text{C}$ ).

cell. Therefore, the sorption equilibrium was reached quickly, within 20 min, and no further sorption was observed thereafter.

Figure 3 shows 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 the figure, biosorption efficiency increases with increase in contact time up to 60 min at  $20\text{--}40^\circ\text{C}$ , after which it is almost constant. Therefore, the optimum contact time was selected as 60 min for further experiments. However, 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  $40^\circ\text{C}$  during a 60 min contact time. This result indicated the exothermic nature of Pb(II) and Cd(II) biosorption onto *C. racemosa* biomass.

A decrease in the biosorption of Pb(II) and Cd(II) ions with the increase in temperature may be due to either the damage of active binding sites in the biomass or an increasing tendency to desorb metal ions from the interface to the solution. The optimum solution temperature was selected as  $20^\circ\text{C}$  for further biosorption experiments

### 3.4. Biosorption isotherms

To find out the mechanistic parameters associated with lead and cadmium adsorption, the results obtained by the adsorption experiments were analysed using Langmuir and Freundlich models. The theoretical Langmuir adsorption isotherm model is the best known of all the isotherm models, and describes the adsorption of a solute from a liquid solution. Langmuir adsorption isotherm [9] applied to equilibrium adsorption, assuming monolayer adsorption onto a surface with a finite number of identical sites, is represented as follows:

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

where  $q_e$  is the equilibrium metal ion concentration on the biosorbent ( $\text{mg} \cdot \text{g}^{-1}$ ),  $C_e$  is the equilibrium metal ion concentration in the solution ( $\text{mg} \cdot \text{L}^{-1}$ ),  $q_{\max}$  is the monolayer biosorption capacity of the biosorbent ( $\text{mg} \cdot \text{g}^{-1}$ ), and  $b$  is the Langmuir biosorption constant ( $\text{L} \cdot \text{mg}^{-1}$ ) relating the free energy of biosorption.

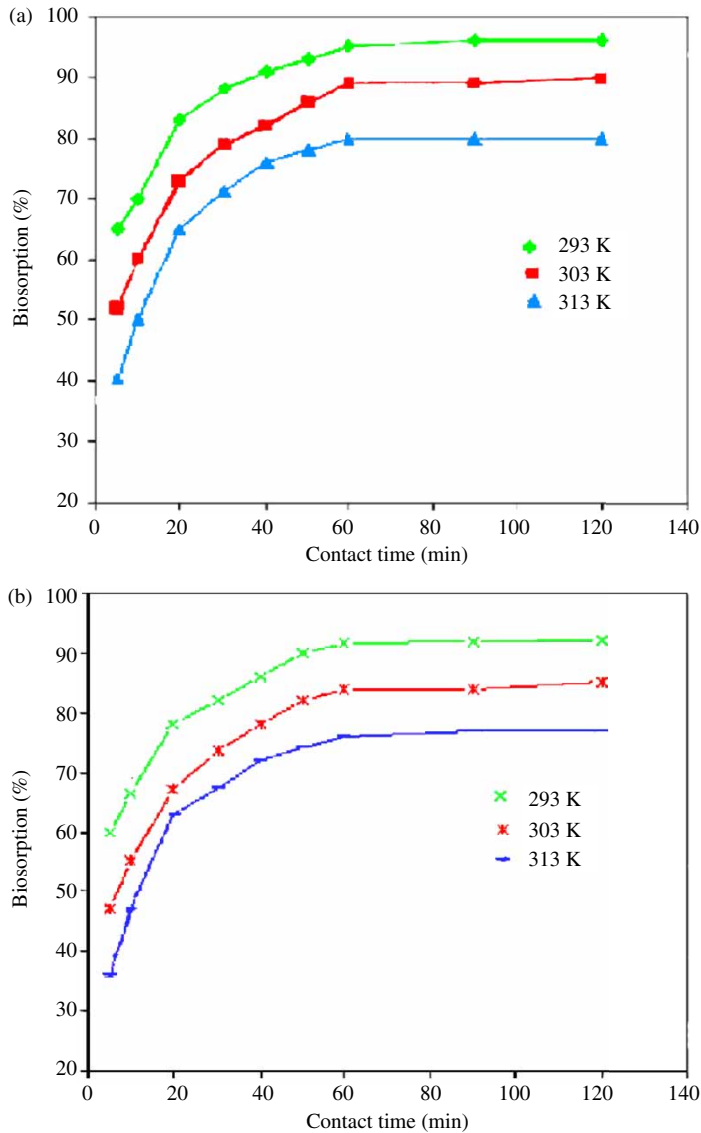


Figure 3. Effect of contact time and temperature on biosorption onto *C. racemosa* (metal concentration,  $10 \text{ mg} \cdot \text{L}^{-1}$ ; biomass dosage,  $20 \text{ g} \cdot \text{L}^{-1}$ ; pH 5). (a) Pb(II), (b) Cd(II).

Linear plots of  $C_e/q_e$  vs.  $C_e$  (Figure 4) were used to determine the value of  $q_{\max}$  ( $\text{mg} \cdot \text{g}^{-1}$ ) and  $b$  ( $\text{L} \cdot \text{mg}^{-1}$ ). The data obtained with the correlation coefficients ( $r^2$ ) are listed in Table 1.

The Freundlich adsorption isotherm is an empirical equation based on adsorption on the heterogeneous surface. The linear form of the Freundlich adsorption isotherm can be defined by the following equation [10]:

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

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 adsorbent required to reduce any initial concentration to predetermined final concentration can be calculated (Figure 5).

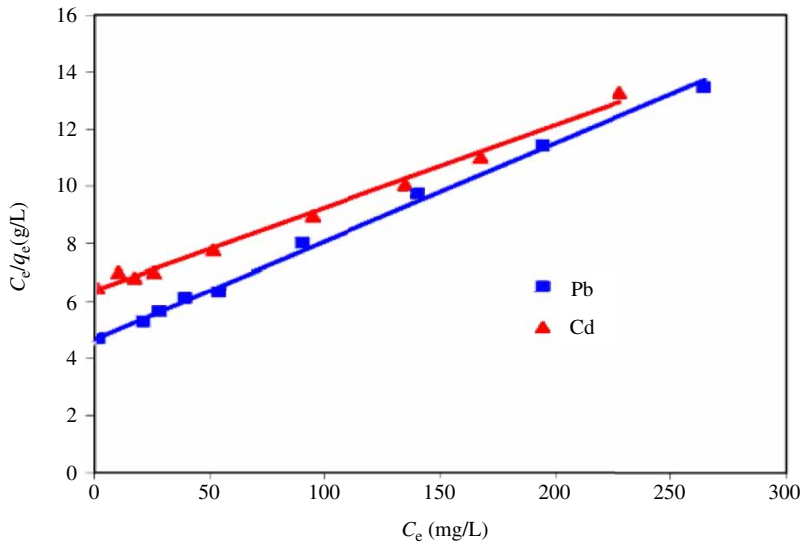


Figure 4. Langmuir isotherm plots for biosorption of Pb(II) and Cd(II) onto *C. racemosa* (biomass dosage,  $20 \text{ g} \cdot \text{L}^{-1}$ ; contact time, 60 min; pH 5; temperature  $20^\circ \text{C}$ ).

Table 1. Adsorption isotherm parameters for Cd(II) and Pb(II) biosorption onto *C. racemosa*.

| Metals | Langmuir constants            |                      |       | Freundlich constants |       |       |
|--------|-------------------------------|----------------------|-------|----------------------|-------|-------|
|        | $q_{\text{max}}(\text{mg/g})$ | $b(\text{L/mg})$     | $r^2$ | $k_f$                | $1/n$ | $r^2$ |
| Cd(II) | 29                            | $7.1 \times 10^{-2}$ | 0.996 | 7.81                 | 0.9   | 0.980 |
| Pb(II) | 34.5                          | $5.2 \times 10^{-2}$ | 0.991 | 10.51                | 0.9   | 0.978 |

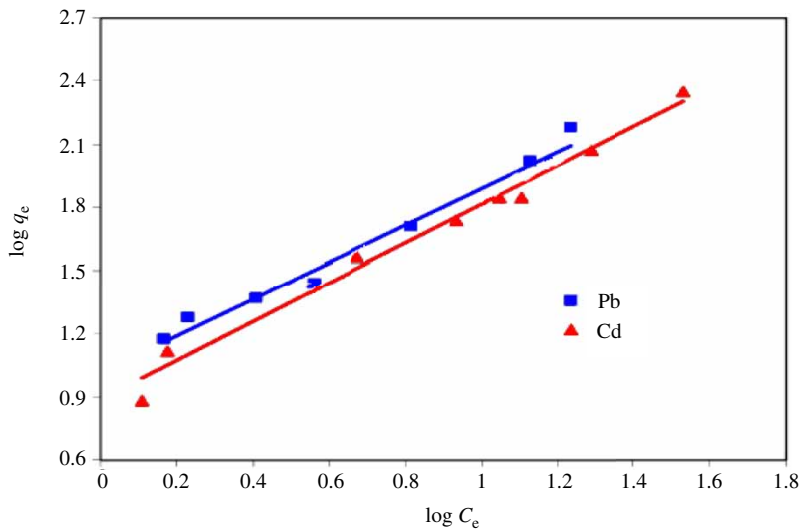


Figure 5. Freundlich isotherm plots for biosorption of Pb(II) and Cd(II) *C. racemosa* (biomass dosage,  $20 \text{ g} \cdot \text{L}^{-1}$ ; contact time, 60 min; pH 5; temperature,  $20^\circ \text{C}$ ).



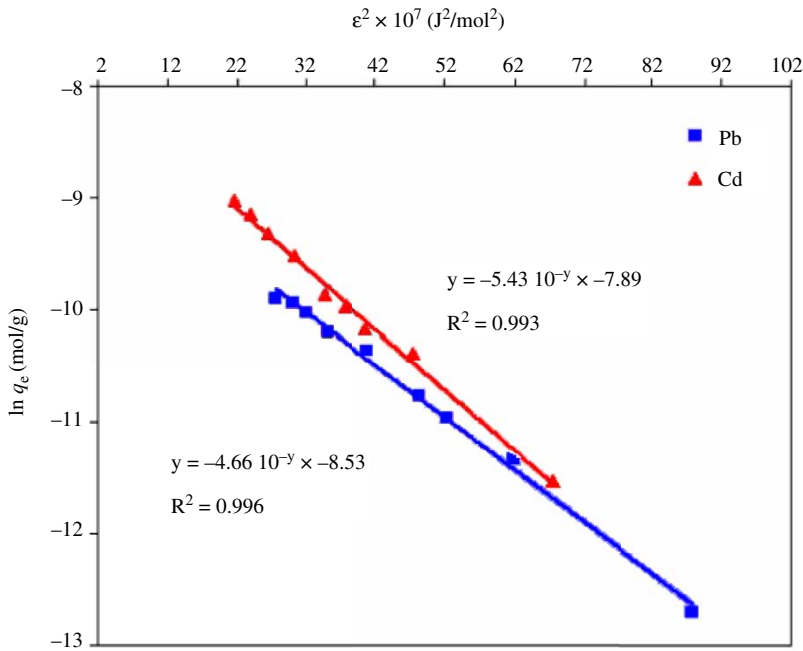


Figure 6. D–R isotherm plots for biosorption of Pb(II) and Cd(II) onto *C. racemosa* biomass (pH 5; biosorbent dosage, 20 g · L<sup>-1</sup>; contact time, 60 min; temperature, 20 °C).

The values for Freundlich constants and correlation coefficients ( $r^2$ ) for the adsorption process are also presented in Table 1. Values of  $n$  between 1 and 10 (i.e.  $1/n < 1$ ) represent a favourable adsorption. Values of  $n$ , which reflect the intensity of adsorption, also reflected the same trend. The  $n$  values obtained for the adsorption process represented a beneficial adsorption.

Table 1 shows that the experimental data are better fitted to the Langmuir [ $r^2 = 0.991$  and  $0.996$  for Pb(II) and Cd(II), respectively] adsorption isotherm than the Freundlich [ $r^2 = 0.978$  and  $0.98$  for Pb(II) and Cd(II), respectively] adsorption isotherm.

The equilibrium data were also subjected to the Dubinin–Radushkevich (D–R) isotherm model to determine the nature of the biosorption processes as physical or chemical. The D–R sorption isotherm is more general than the Langmuir isotherm, as its derivation is not based on ideal assumptions such as the equipotent of the sorption sites, absence of steric hindrance between sorbed and incoming particles and surface homogeneity on microscopic level [11]. The linear presentation of the D–R isotherm equation [12] is expressed by

$$\ln q_e = \ln q_m - \beta \varepsilon^2, \quad (4)$$

where  $q_e$  is the amount of metal ions adsorbed on per unit weight of biomass ( $\text{mol} \cdot \text{g}^{-1}$ ),  $q_m$  is the maximum biosorption capacity ( $\text{mol} \cdot \text{g}^{-1}$ ),  $\beta$  is the activity coefficient related to biosorption mean free energy ( $\text{mol}^2 \cdot \text{J}^{-2}$ ) and  $\varepsilon$  is the Polanyi potential [ $\varepsilon = RT \ln(1 + \frac{1}{C_e})$ ].

The D–R isotherm model fitted the equilibrium data well because the  $R^2$  value was found to be 0.993 for Pb(II) biosorption and 0.997 for Cd(II) biosorption (Figure 6). From the intercept of the plots, the  $q_m$  value was found to be  $2.0 \times 10^{-4} \text{ mol} \cdot \text{g}^{-1}$  for Pb(II) biosorption and  $3.7 \times 10^{-4} \text{ mol} \cdot \text{g}^{-1}$  for Cd(II) biosorption. The biosorption mean free energy ( $E$ ,  $\text{kJ} \cdot \text{mol}^{-1}$ ) is as follows:

$$E = \frac{1}{\sqrt{-2\beta}}. \quad (5)$$

The  $E$  ( $\text{kJ} \cdot \text{mol}^{-1}$ ) value gives information about the adsorption mechanism, physical or chemical. If it lies between 8 and  $16 \text{ kJ} \cdot \text{mol}^{-1}$ , the adsorption process takes place chemically and if  $E < 8 \text{ kJ} \cdot \text{mol}^{-1}$ , the adsorption process proceeds physically [13]. The mean biosorption energy was calculated as 10.4 and  $9.6 \text{ kJ} \cdot \text{mol}^{-1}$  for the biosorption of Pb(II) and Cd(II) ions, respectively.

These results indicated that the biosorption processes of both metal ions onto *C. racemosa* biomass may be carried out via chemisorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate [14].

### 3.5. Adsorption kinetics study

The study of adsorption kinetics describes the solute uptake rate and evidently these rates control 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 [15]. 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 analysed using pseudo-first-order [16] and pseudo-second-order models [17].

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

The pseudo-first-order kinetic model was proposed by Lagergren [16]. The integral form of the model is generally expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \quad (6)$$

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

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

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

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{t}{q_2}, \quad (7)$$

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.

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

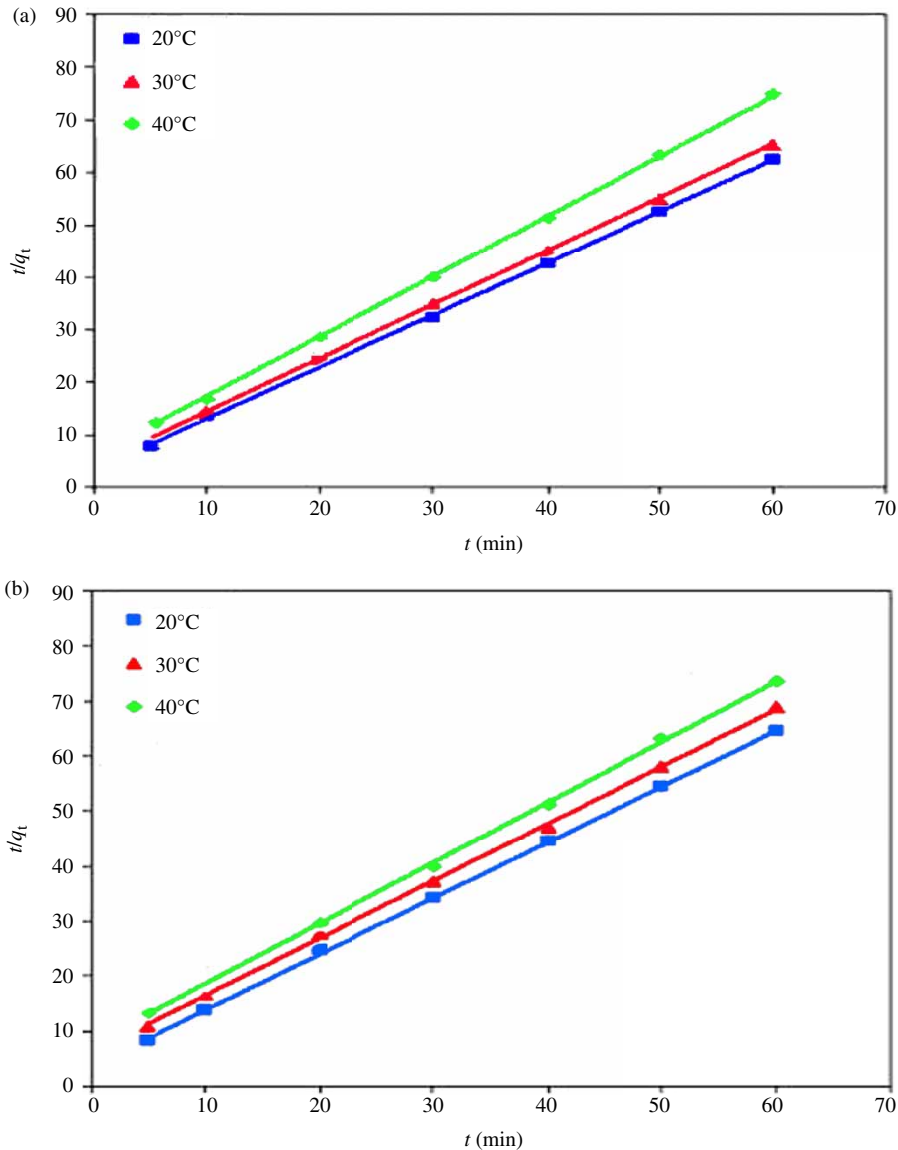


Figure 7. Pseudo-second-order kinetic plots at different temperatures: (a) Pb(II) biosorption, (b) Cd(II) biosorption.

where  $k_2$  ( $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ ) is the rate constant of adsorption,  $q_2$  is maximum adsorption capacity ( $\text{mg} \cdot \text{g}^{-1}$ ) [18]. The values of  $k_1$ ,  $q_e$  and  $k_2$ ,  $q_2$  were obtained from the slopes and intercepts of plots of  $\log(q_e - q_t)$  vs.  $t$  and  $t/q_t$  vs.  $t$  at different temperatures.

Linear plots of  $t/q_t$  vs.  $t$  for the pseudo-second-order model for the biosorption of Pb(II) and Cd(II) ions onto the alga biomass at 20–40 °C are shown in Figure 7a and b, respectively.

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 are given in Table 2.

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

### 3.6. Thermodynamic parameters

Thermodynamic parameters such as Gibbs free energy change,  $\Delta G^0$ , standard enthalpy change,  $\Delta H^0$ , and standard entropy change,  $\Delta S^0$ , were also found to give more information about the nature of sorption process [19]. The thermodynamic parameters were calculated by the following equations:

$$\ln k_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (\text{Van't Hoff equation}), \quad (8)$$

$$\Delta G^0 = -RT \ln k_c, \quad (9)$$

where  $k_c = (q_e/C_e)$  is the adsorption equilibrium constant,  $T$  is the absolute temperature (K), and  $R$  is the gas constant. When  $\ln k_c$  versus  $1/T$  is plotted (Figure 8),  $\Delta H^0$  and  $\Delta S^0$  can be computed from the slope and intercept of the Van't Hoff equation. The calculated parameters are given in Table 3.

The negative  $\Delta G^0$  values indicated the thermodynamically feasible and spontaneous nature of the biosorption. The decrease in  $\Delta G^0$  value with increase in temperature shows a decrease in feasibility of biosorption at higher temperatures.

The negative  $\Delta H^0$  is an indicator of the exothermic nature of the biosorption and its magnitude also gives information on the type of biosorption, which can be either physical or chemical. Therefore, the  $\Delta H^0$  values showed that the biosorption processes of Pb(II) and Cd(II) ions onto

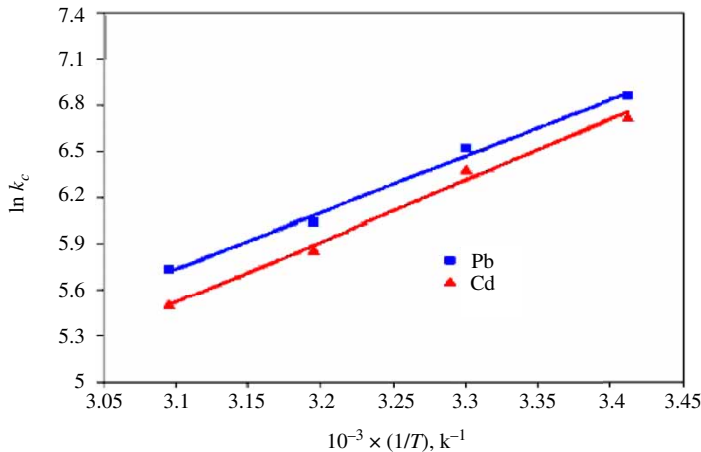


Figure 8. Determination of thermodynamic parameters for biosorption of Pb(II) and Cd(II) onto *C. racemosa* biomass.

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

| T (k)  | $\Delta G^0$ (kJmol <sup>-1</sup> ) | $\Delta H^0$ (kJmol <sup>-1</sup> ) | $\Delta S^0$ (Jmol <sup>-1</sup> k <sup>-1</sup> ) |
|--------|-------------------------------------|-------------------------------------|--|
| Cd(II) |                                     |                                     |  |
| 298    | -16.3                               |                                     |  |
| 308    | -16                                 | -32.8                               | -55.8  |
| 318    | -15.2                               |                                     |  |
| Pb(II) |                                     |                                     |  |
| 298    | -16.7                               |                                     |  |
| 308    | -16.4                               | -30.1                               | -45.7  |
| 318    | -15.6                               |                                     |  |

*C. racemosa* biomass took place via chemisorption. The mean biosorption energy values obtained from the D–R model also confirm this result. The  $\Delta S^0$  parameter was found to be  $-45.7 \text{ J} \cdot \text{mol}^{-1} \text{ K}$  for Pb(II) biosorption and  $-55.8 \text{ J} \cdot \text{mol}^{-1} \text{ K}$  for Cd(II) biosorption. The negative  $\Delta S^0$  value suggests a decrease in the randomness at the solid/solution interface during the biosorption process [20–23].

### 3.7. FTIR analysis

The functional group is one of the keys to understanding the mechanism of metal binding on the algal surface. FTIR was used to analyse the functional groups in the fresh-dried algal biomass. The results of FTIR transmission spectra are shown in Table 4. Several functional groups were found in the structure of *C. racemosa* such as carboxylic acid, amine, amide, amino, sulfonyl and sulfonate groups. In comparing pristine and metal-loaded algal biomass, it was observed that there was a shift ( $>14 \text{ cm}^{-1}$ ) in the wave number of the 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 [24]. 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  $1420 \text{ cm}^{-1}$  for two heavy metals, whereas the other groups did not seem to have shifts in the wave number of the peak. These results indicated that there was a high potential that O–H bending groups from carboxylic acid are involved with heavy metal binding.

For the amine group, there were changes in wave number for N–H stretching in the  $\text{Cd}^{2+}$  sorptions. C–N stretching was found to disappear with the sorptions of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ . The N–H bending group did not seem to change for either metal. These results could be interpreted as N–H stretching in amine group being associated with  $\text{Cd}^{2+}$  sorption, and C–N stretching for sorption of both metals. By contrast, N–H bending was thought not to be involved in metal binding by this biomass.

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

|                 | Pristine | $\text{Cd}^{2+}$ loaded | $\text{Pb}^{2+}$ 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<br>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                     |

Table 5. Comparison of adsorption capacity of *C. racemosa* biomass for Pb(II) and Cd(II) with that of other adsorbents.

| Adsorbents                     | Biosorption capacity (mg/g) |        | Reference     |
|--------------------------------|-----------------------------|--------|---------------|
|                                | Pb(II)                      | Cd(II) |               |
| Calcite                        | 19.92                       | 18.52  | [25]          |
| Olive cake                     | 19.53                       | 10.56  | [26]          |
| Wheat bran                     | 62                          | 21     | [27]          |
| <i>Amanita rubescens</i>       | 38.4                        | 27.3   | [21]          |
| <i>Lactarius scrobiculatus</i> | 56.2                        | 53.1   | [20]          |
| <i>Caulerpa racemosa</i>       | 34.5                        | 29     | Present study |

Observations for the amide group revealed that N–H stretching was shifted slightly by Cd<sup>2+</sup> sorption from 3410 to 3396 cm<sup>-1</sup>. N–H stretching was also affected by the sorption of Pb<sup>2+</sup> where the new peak occurred at a wave number of 3340 cm<sup>-1</sup>. In 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<sup>2+</sup>. 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. By contrast, C–O in the amino group seemed to play an important role for all metal sorption because 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<sup>2+</sup>, and Pb<sup>2+</sup>. The S=O stretching in the sulfonyl and sulfonate groups was involved with two metal sorptions because there was a shift in sulfonate peak at 1370 cm<sup>-1</sup> to sulfonyl at 1389 cm<sup>-1</sup>. S–O stretching was not associated with the sorption of Cd<sup>2+</sup> and Pb<sup>2+</sup>.

### 3.8. Comparison of Pb(II) and Cd(II) removal with different adsorbents reported in the literature

The adsorption capacity of *C. racemosa* biomass for Pb(II) and Cd(II) has been compared with other adsorbents reported in the literature and the adsorption capacities are presented in Table 5. Values are reported in the form of monolayer adsorption capacity.

Adsorption capacity varies and depends on the characteristics of the individual adsorbent, the extent of surface/surface modification and the initial concentration of the adsorbate. As can be seen from Table 5, the adsorption capacity of *C. racemosa* for Pb(II) and Cd(II) was found to be comparable and moderately higher than those of other sorbent materials reported in literature. Therefore, it can be noteworthy that the *C. racemosa* biomass has a great potential for the removal of Pb(II) and Cd(II) ions from aqueous solution.

## 4. Conclusion

In this study, batch adsorption experiments for the removal of Cd(II) and Pb(II) from aqueous solutions were carried out using algal biomass (*C. racemosa*). The adsorption characteristics were 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 found to be 34.5 and 29 mg · g<sup>-1</sup> ions, respectively. From the D–R isotherm model, the mean free energy was calculated as 10.4 kJ · mol<sup>-1</sup> for Pb(II) biosorption and 9.6 kJ · mol<sup>-1</sup> for Cd(II) biosorption, indicating that the biosorption of both metal ions took by chemisorption. Experimental data obtained from rate kinetics were better described by a pseudo-second-order model than a pseudo-first-order model,

as evident from correlation coefficient values ( $r^2$ ). The calculated thermodynamic parameters ( $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$ ) 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 study has illustrated an alternative solution for the management of unwanted biological materials where *C. racemosa*, a fast-growing marine algae, could be, to some extent, utilised as a biosorbent for the removal of heavy metals from low-strength wastewater.

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