

Adsorptive removal of cadmium from aqueous media using *Posidonia oceanica* biomass: equilibrium, dynamic and thermodynamic studies

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Abstract *Posidonia oceanica* (L.), a marine biomass, has been used as an effective and efficient biosorbent for the removal of Cd(II) from aqueous media. The physico-chemical properties of biosorbent were investigated by elemental analysis, BET surface area, FT-IR, SEM and EDX methods before and after adsorption. Batch adsorption experiments were carried out to investigate the effects of solution pH, dosage of biosorbent, contact time and temperature. The biosorbent exhibited the maximum uptake of 58.82 mg/g under the optimal adsorption condition. Kinetics experiments indicated that the pseudo-second-order model displayed the best correlation with adsorption kinetics data. Besides, experimental data could be better described by the Langmuir isotherm model. Desorption experiments were carried out to explore the feasibility of regenerating the biosorbent. The regeneration efficiency was 96.03 % using desorption agent of 0.2 M HCl. The thermodynamic parameters (ΔH^0 , ΔS^0 and ΔG^0) of the cadmium ion uptake onto P.O indicated that the process is endothermic and proceeds spontaneously. The findings of the present study indicate that P.O can be successfully used for separation of Cd(II) from aqueous solutions. The results suggested that the adsorbent is

promising for use as an effective and economical adsorbent for Cd(II) ions removal.

Keywords Biosorption · Cadmium · *Posidonia oceanica* · Kinetics · Isotherms · Thermodynamics · Desorption

Introduction

The discharge of heavy metal from industries into environment has resulted in a number of environmental problems. These heavy metal ions pose a hazard to public health and environment when discharged inappropriately (Laus et al. 2010). Cadmium is attracting wide attention of environmentalists as one of the most toxic heavy metals. The major sources of cadmium release into the environment by waste streams are electroplating, smelting, alloy manufacturing, pigments, plastic, battery, mining and refining processes (Tsezos 2001). The harmful effects of cadmium include number of acute and chronic disorders such as “itai-itai” disease, renal damage, emphysema, hypertension and testicular atrophy (Leyva-Ramos et al. 1997).

Considerable research has been carried out in developing cost-effective heavy metal removal techniques. Physicochemical methods, such as chemical precipitation, chemical oxidation or reduction, filtration, electrochemical treatment, application of membrane technology, evaporation recovery, solvent extraction and ion-exchange processes, have been traditionally employed for heavy metal removal from industrial wastewater. However, these techniques may be ineffective or extremely expensive, especially when the metals are dissolved in large volumes of solution at relatively low concentrations (around 1–100 µg/mL) (Valdman and Leite 2000). Removal of

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Cd(II) ions from wastewater by adsorption has been investigated by many researchers. The main advantages of the adsorption are less sludge volume produced and simple design. Because the metal ions can be faster brought to the external and internal binding sites in the adsorptive membrane than those of adsorptive beads, research about the adsorptive membrane is gaining more and more attention (Liu and Bai 2006).

In recent years, increased attention has been focused on the use of naturally available low-cost biomaterials for removing heavy metal ions from wastewater (Wang et al. 2008). Use of biomaterials makes the adsorption process more environmental friendly.

We are interested in one of the most abundant marine plants: *Posidonia oceanica* (P.O) an endemic marine Magnoliophyta found in the Mediterranean Sea. The valorization of this available and renewable lignocellulosic biomass can be considered as a suitable solution for the removal of Cd(II) from aqueous media.

In the present study, the dead leaves of *P. oceanica* were collected from the coast of Jijel (East of Algeria) in December 2010. A simple and economic preparation of the biosorbent was performed, and biosorption experiments have been conducted to determine the metal biosorption mechanism. The main objectives of the present study include: (1) to characterize the biosorbent through FTIR, XRD, SEM-EDX, BET surface area and elemental analysis to know its chemical, (2) to study the sorption potential of P.O for Cd (II) removal from water under different operational conditions and (3) to understand the kinetic mechanism. The data from the experiments were fitted with different isotherm models. The reusability of the P.O is also investigated.

Materials and methods

Biosorbent preparation

Plant materials were collected from the Jijel coast (East of Algeria). Samples were washed several times using distilled water to remove extraneous and salts. They were then dried in an oven at 60 °C for 48 h. The dried samples were ground, and the powder was sieved through different sizes and 0.3–0.5 mm fraction and finally stored in a desiccator and used in further experiments.

Chemicals and equipments

All reagents used were of AR grade. Distilled water was used throughout the experimental studies. Stock solution

(1,000 mg/L) was prepared by dissolving $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. This was further diluted to obtain the desired concentration for practical use. ACS reagent grade HCl, NaOH and buffer solutions (E. Merck) were used to adjust the solution pH. A WTW (270) pH meter was used for pH measurements. The pH meter was calibrated using buffer standard solutions of pH 4.0, 7.0 and 9.2. Fourier transform infrared spectrophotometer (Shimadzu, 8400 s) was used to analyze the organic functional groups of the biosorbent. Elemental analyzer (EA 1100) was used for elemental analysis of the P.O. For BET-specific surface area estimation, a porosimeter (ASAP 2010) was used. The metal concentrations in the samples were determined using atomic absorption spectrophotometer (Shimadzu, 6200 AA). Wide-angle X-ray diffraction (WAXD) patterns of powder P.O sample were recorded on an X-ray diffractometer (D8-ADVANCE), by using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 30 mA. Scanning electron microscopy (Quanta 200) was used to study the surface morphology of the biosorbent.

Biosorption studies

In order to optimize the experimental conditions, the batch studies were performed for different metal concentrations (10–100 mg/L), contact times (0–90 min), pH (2–8), biomass dosages from (1 to 5 g/L) and temperature (285–328 K). For the adsorption isotherm studies, the initial metal ion concentration was varied over a range of 20–250 mg/L. The solutions including the metal ions and biosorbent were shaken during optimum contact time in a mechanical shaker at 150 rpm. After the contents of the flask were filtered through Whatman no. 42 filter papers, the metal concentrations of filtrate were analyzed using AAS.

The sorption capacity of metal ion is the concentration of metal ion on the biosorbent, and it can be calculated based on the mass balance principle where

$$q_t = \frac{(C_0 - C_{\text{res}}) \cdot V}{m} \quad (1)$$

where C_0 is the initial cadmium(II) concentration (mg/L), C_{res} is the residual cadmium(II) concentration at any time (mg/L), V is the volume of solution (L) and m is the mass of the sorbent (g). At equilibrium, C_{res} is equal to C_{eq} and q is equal to q_{eq} .

Desorption and reusability

Desorption of Cd(II) ions was performed using 0.2 M HCl solution as a desorbing agent to estimate the reversibility of



P.O and recovery of Cd(II) ions. Experiments were carried out as follows: The P.O was equilibrated with 100 mg/L Cd(II) solution followed by its desorption with the required solution at 25 °C, with a shaking speed of 150 rpm for 80 min. Then, the P.O sample was washed with distilled water several times and subjected again to four successive adsorption–desorption cycles.

Results and discussion

Characterization of the biosorbent

Characterization of biosorbent surface and structure holds keys to understanding the metal binding mechanism onto biomass. From elemental analysis results, it was identified that P.O is composed of 40.95 % carbon, 5.56 % hydrogen, 1.22 % nitrogen, 2.98 % sulfur and 32.63 % oxygen. Sulfur groups, which are soft bases, have chemical affinity toward metal ions (Reddy et al. 2012), and presence of sulfur in P.O qualifies it as a potential biosorbent.

FTIR spectra

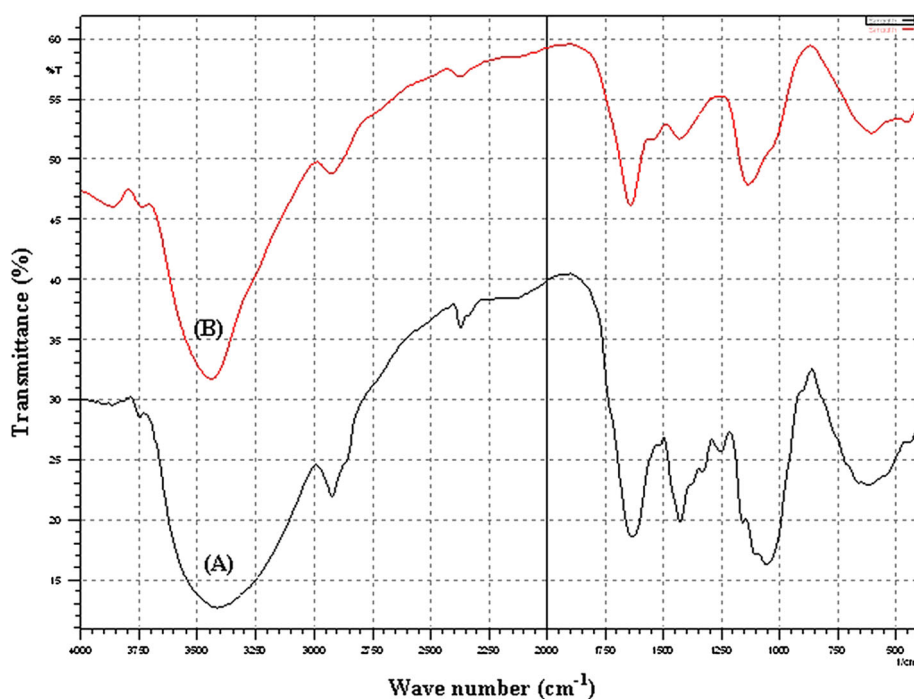
The FTIR spectra of *P. oceanica* showed the presence of many functional groups, indicating the complex nature of the biosorbent. The infrared spectrum, shown in Fig. 1a, displays a number of absorption peaks. The large band around 3,600–3,100 cm^{-1} (with maximum absorption at 3,445 cm^{-1}) is indicative of the existence of hydroxyl

(–OH) groups. The spectrum also displays an absorption peak at 2,918 cm^{-1} , corresponding to the –CH₂ group bound by stretching of the –OH groups. The peak at 1,640 cm^{-1} is characteristic of carbonyl group stretching from aldehydes and ketones. These groups could be conjugated or nonconjugated to aromatic rings (Kellner et al. 1998). A 1,423 cm^{-1} stretching of phenolic –OH and C–O, and a 1,046 cm^{-1} vibration peak of aliphatic C–O bands <1,000 cm^{-1} observed in the fingerprint region was assigned to phosphate and sulfur groups (Coates 2000). Figure 1b shows the spectrum of P.O biomass after the biosorption of Cd(II). FTIR spectrum shows the shift in peaks at wave number 3,445 to 3,455 cm^{-1} . The change in hydroxyl group after biosorption shown in Fig. 1b indicated that it had been changed from multimer to monopolymer or even dissociative state (Kellner et al. 1998) which showed that the degree of hydroxyl polymerization in lignocellulose was decreased by binding of Cd(II). The spectrum after interaction with Cd(II) showed disappearance of asymmetrical stretching band at 1,430 cm^{-1} when compared with that observed in the spectra of P.O. These results indicated that the biosorption of Cd(II) occurs at hydroxyl, carboxyl and carbonyl functional groups present on the surface of *P. oceanica*.

SEM and SEM-EDAX analysis

Scanning electron microscopy was used for characterizing the morphology and structure of the biosorbent.

Fig. 1 FTIR spectra of: (A) P.O; (B) Cd-loaded P.O



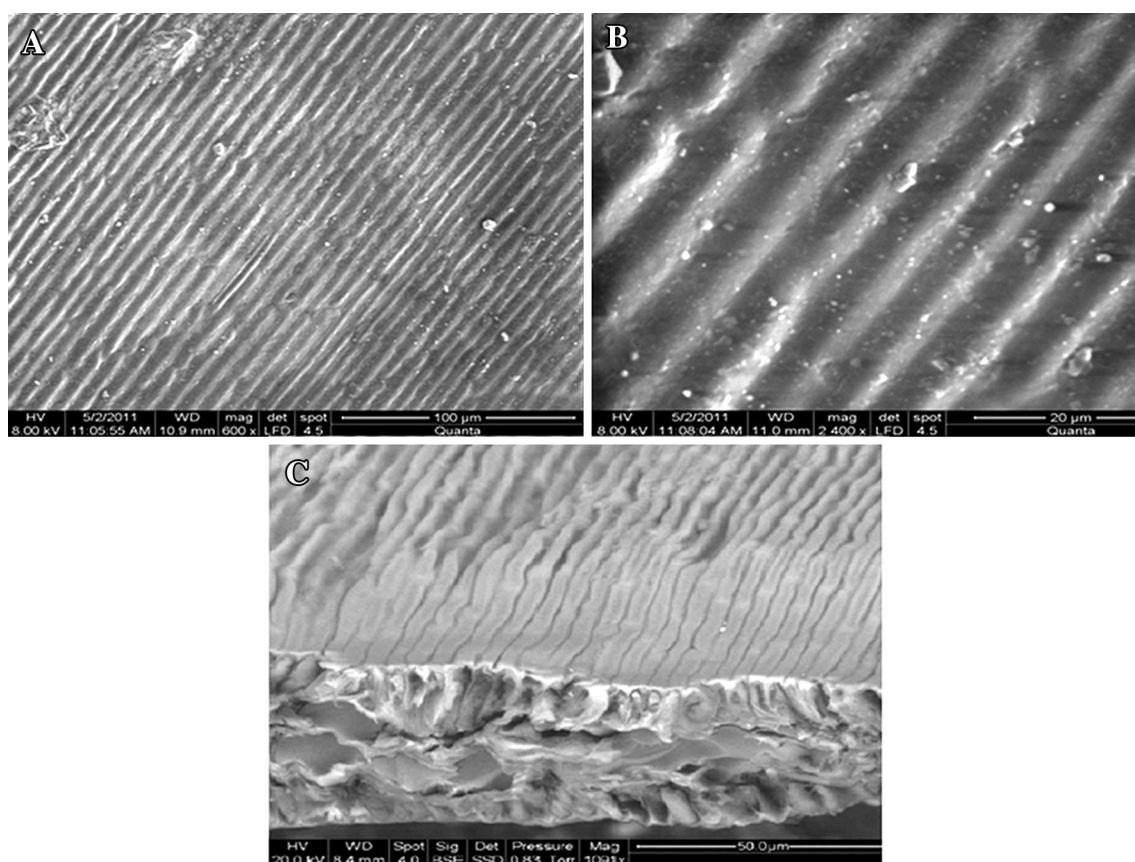


Fig. 2 SEM photographs of P.O [scale bar 100 μm (a), 20 μm (b), 50 μm (c)]

Figure 2a, b shows the surface morphology of the biomass. This is a very structured material characterized by a “fibrous” aspect. This is confirmed by Fig. 2c that shows the presence of lamellar structures on the external layers, while the central part of the ribbon-like material is characterized by a less-structured aspect. The surface morphology offers a more favorable area than a smooth-surface material.

Additionally, Fig. 3a, b shows the SEM-EDAX analyses of the biosorbent before and after Cd(II) sorption. The analyzed surface covers the whole external surface of the biomass shown on the SEM photographs. On the raw material, the most representative elements (apart of carbon or oxygen) are Ca, Mg, Fe, Na and K. After Cd(II) sorption, Na and K elements disappeared and they are replaced by Cd(II). This could indicate that metal binding occurs through ion exchange. The phase-contrast photograph of Cd(II)-loaded biosorbent (not shown) does not indicate the presence of metal aggregates at the surface of the material. This means that the metal is probably bound uniformly at

the surface of the biosorbent without occurrence of micro-precipitation.

X-ray diffraction

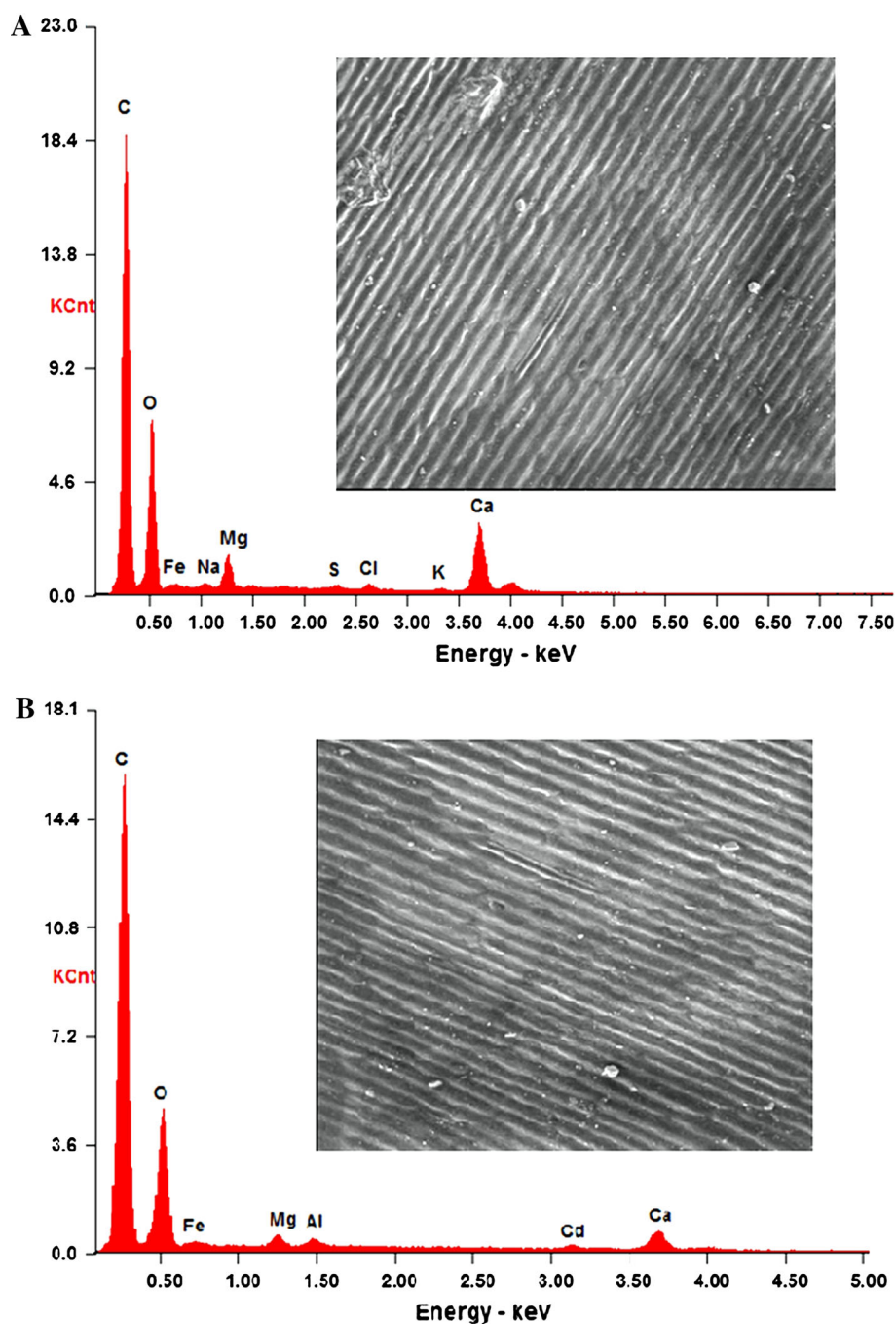
XRD pattern of the P.O (Fig. 4) does not show very sharp peaks and more or less looks amorphous. The peaks at 2θ values of 17.48, 28.27, 41.86 and 44.55 corroborate the presence of CaSO_4 , CaCl_2 , Fe_3O_4 and MgFeSiO_4 , respectively.

pH effect on Cd(II) sorption

Hydrogen ion concentration is considered as one of the most important parameters that influences the adsorption behavior of metal ions in aqueous solutions. It affects the solubility of the metal ions in the solution and the degree of ionization of the adsorbate during the reaction (Mansour et al. 2011; Nomanbhay and Palanisamy 2005). The pH level affects the network of negative charge on the surface



Fig. 3 SEM-EDX analysis of P.O (a before Cd(II) sorption, b after Cd(II) sorption)



of the biosorbing cell walls, as well as physicochemistry and hydrolysis of the metal. Therefore, preliminary experiments (contact time of 90 min, biosorbent weight of 5 g/L and cadmium concentration of 100 mg/L) have been performed to find out the optimum pH for maximizing the metal removal. Uptake removal of the cadmium ions as a function of pH is shown in Fig. 5. It has been observed that under highly acidic conditions (pH = 2.0), the amount of

Cd(II) removal was very small, while the sorption had been increased with the increase in pH from 3 to 6 and then decreased in the range 7 and 8. The lower removal efficiency at low pH is apparently due to the presence of higher concentration of H^+ in the solution which compete Cd(II) ions for the adsorption sites of the P.O. With increase in pH, the H^+ concentration decreases leading to increased Cd(II) uptake.



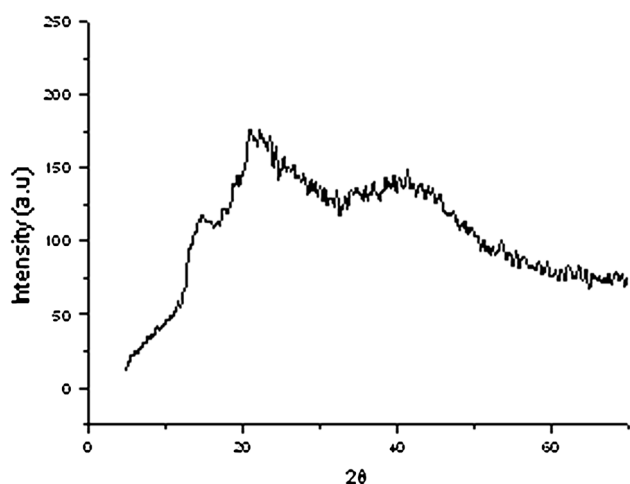


Fig. 4 XRD spectrum of P.O

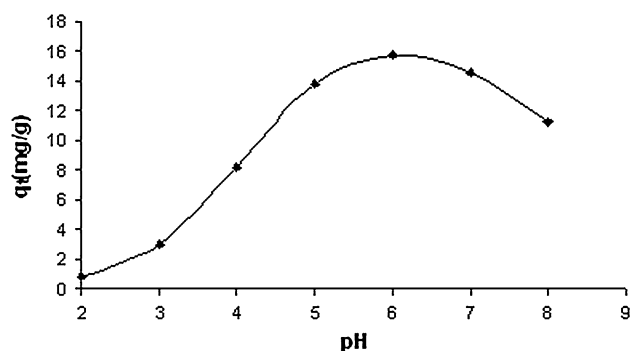
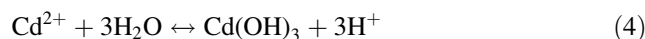
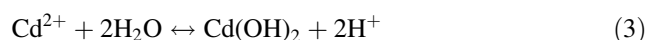
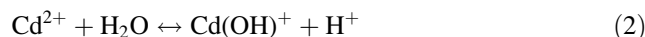


Fig. 5 Effect of pH on the sorption of Cd(II) by P.O

The point of zero charge (PZC) of biosorbent was determined according to the procedure described by (Lua et al. 2009): 100 mL of distilled water was added to an Erlenmeyer flask, which was then capped with cotton. The distilled water was heated until boiling for 20 min to eliminate CO₂ dissolved in water. Once stopped heating, this flask should be capped immediately to prevent CO₂ dissolving in water again. On the other hand, 0.2 g of adsorbent was placed in a 25 mL Erlenmeyer flask to which 15 mL of CO₂-free water was added. The flask was sealed with a rubber stopper and left in continuous agitation for 48 h at room temperature. Then, pH of filtrate was measured, and this value is point of zero charge.

At pH below 5.28 (PZC), the surface of P.O would be positively charged due to protonation. This protonation effect was more pronounced at lower pH values due to the presence of higher concentration of H⁺ ions in the solution, which resulted in more unfavorable Cd(II) biosorption. At the optimum pH value (pH 6.0), the surface of the P.O is negatively charged and favorable to the biosorption of

Cd(II). Decreased biosorption at higher pH (pH > 6) was due to the formation of soluble hydroxylated complexes of the metal ions and their competition with the active sites, and as a consequence, the retention had been decreased again. Therefore, further experiments were carried out with initial pH value of 6. Previous studies also reported that the maximum biosorption efficiency for Cd(II) metal ion on biomass was observed at pH 6 (Chen et al. 2012). With the rise in pH, fewer H⁺ ions exist, and consequently, Cd(II) ions have a better chance to bind to free binding sites. Later, when the pH enters basic conditions (Eqs. 2–4), the formation of Cd(OH)₃[−] takes place due to the dissolution of Cd(OH)₂, and as a result, the adsorption rate decreases (Reddy et al. 2012).



Effect of adsorbent dosage on adsorption

Biosorption of Cd(II) onto P.O was studied by changing the quantity of biosorbent from 1 to 5 g/L in the test solution while maintaining the initial concentration 100 mg/L, pH 6 and contact time of 40 min constant. When the biosorbent dosage increased from 1 to 5 g/L, the removal percentage of Cd(II) ions increased from 10.15 to 78.45 %; however, the uptake capacity of P.O decreased from 17.97 to 4.31 mg/g. The obtained results indicated that the cadmium removal efficiency increased but adsorption density decreased with an increasing of adsorbent dosage. The decrease in adsorption density is attributed to some of the adsorptive sites that remained unsaturated during the adsorption process, whereas the number of available adsorptive sites increased with more adsorbent, and this results in better removal efficiency. Based on removal percentage of Cd(II) ions from aqueous solution, an adsorbent dosage of 5 g/L was selected for further experiments.

Effect of contact time and biosorption kinetics

For practical applications, the process design and operation control, the sorption kinetics is very important. Sorption kinetics in wastewater treatment was significant, as it provides valuable insights into the reaction pathways and the mechanism of the sorption reactions (Reddy et al. 2011). Effect of contact time on adsorption behavior was studied in different time intervals ranging from 0 min to 90 min, solution pH of 6.0, an adsorbent dosage of 5 g/L and initial Cd(II) ions concentration of 50 and 100 mg/L,



respectively. It is shown that Cd(II) ions adsorption on the P.O was encouraging, where about 80 % of the adsorption took place within the first 15 min and equilibrium was attained within 30 min. This is attributed to a large number of vacant surface adsorptive sites that are available for adsorption during the initial stage, and with the lapse of time, the remaining vacant surface adsorptive sites are difficult to be occupied by Cd(II) ions due to repulsive forces between Cd(II) ions adsorbed on the adsorbent and bulk phases. As a result, the adsorption experiments in the other parts were carried out for 30 min.

Biosorption kinetics

Biosorption kinetics depends on the sorbate–biosorbent interactions and operating conditions. Several kinetic models are available to understand the behavior of the adsorbent and also to examine the controlling mechanism (Sari and Tuzen 2009). In this study, the biosorption equilibrium data were analyzed using three kinetic models including pseudo-first-order, pseudo-second-order and intraparticle diffusion model.

The linear form of the pseudo-first-order rate equation (Lagergren 1898) is given as

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (5)$$

where q_t and q_e (mg/g) are the amounts of the Cd(II) ions sorbed at equilibrium (mg/g) and t (min), respectively, and k_1 is the rate constant of the equation (min^{-1}). The biosorption rate constants (k_1) can be determined experimentally by plotting $\log(q_e - q_t)$ versus t .

Experimental data were also tested by the pseudo-second-order kinetic model, which is given in the following form (Ho and McKay 1999)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

where k_2 (g/mg min) is the rate constant of the second-order equation, q_t (mg/g) is the amount of biosorption time t (min) and q_e is the amount of biosorption equilibrium (mg/g). The biosorption rate constants (k_2) can be determined experimentally by plotting of t/q_t versus t . The initial adsorption rate h_0 (mg/g min) is defined as

$$h_0 = k_2 q_e^2 \quad (7)$$

The experimental results were also analyzed in terms of intraparticle diffusion model to investigate whether the intraparticle diffusion is the rate-controlling step in biosorption of Cd(II) onto P.O biomass. The intraparticle

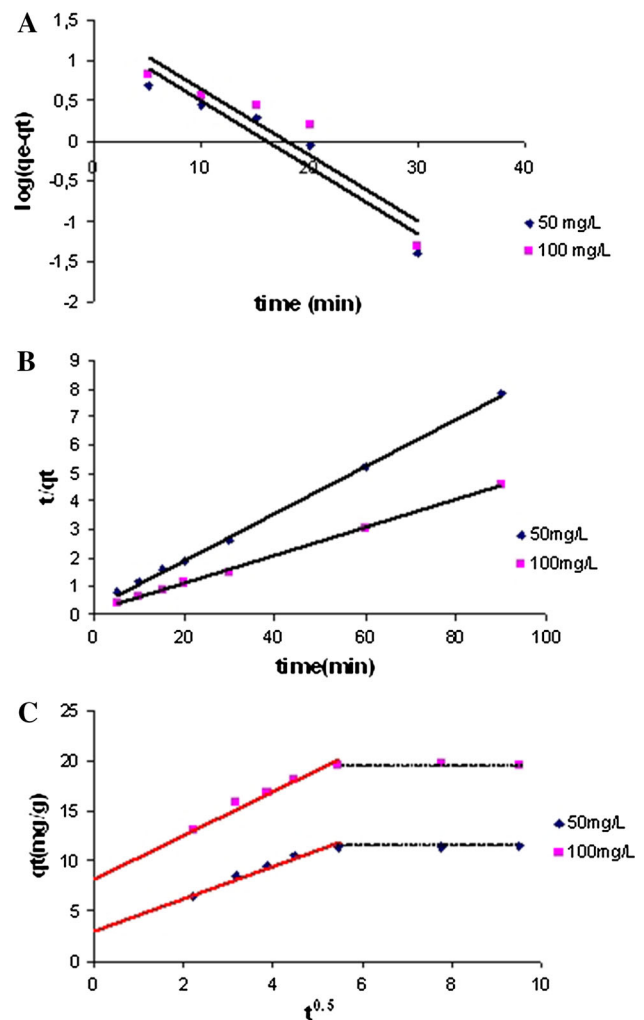


Fig. 6 Kinetics plots for the sorption of Cd(II) onto P.O (a pseudo-first order, b pseudo-second order, c intraparticle diffusion) at pH 6

diffusion equation is expressed as (Weber and Morris 1963)

$$q_t = k_{id} t^{0.5} \quad (8)$$

where k_{id} intraparticle diffusion rate constant ($\text{mg/g min}^{0.5}$). According to this model, the plot of uptake (q_t) versus the square root of time should be linear if intraparticle diffusion is involved in the adsorption process, and if these lines pass through the origin, then intraparticle diffusion is the rate-controlling step.

For the Lagergren's first-order kinetic model, a plot of $\log(q_e - q_t)$ against t according to Eq. (5) should give a straight line to confirm the applicability of the kinetic model. In a true first-order process, $\log q_e$ should be equal to the intercept of a plot of $\log(q_e - q_t)$ against " t " (Fig. 6a). From the results in Table 1, it is observed that



Table 1 The pseudo-first-order and pseudo-second-order and Weber and Morris constants

Initial Cd(II) concentration (mg/L)	$q_{e,exp}$	Pseudo-first order			Pseudo-second order				Weber and Morris		
		$q_{e,cal}$	k_1	R^2	$q_{e,cal}$	k_2	h_0	R^2	$q_{e,cal}$	k_{id}	R^2
50	8.24	10.11	0.201	0.96	8.30	0.047	3.23	0.99	13.80	2.52	0.81
100	15.69	20.10	0.168	0.97	15.70	0.021	5.17	0.99	21.47	3.92	0.86

the theoretical values ($q_{e,cal}$) were far lower than those of the experimental data $q_{e,exp}$ and low correlation coefficient values obtained for the pseudo-first-order model indicated that sorption does not occur exclusively on one site per ion.

The pseudo-second-order model was developed based on the assumption that the rate-limiting step may be chemisorption promoted by either valence forces, through sharing of electrons between the biosorbent and sorbate, or covalent forces, through the exchange of electrons between the parties involved (Ho and McKay 1999). A plot of “ t/q_t ” versus “ t ” should give a linear relationship for the applicability of the second-order kinetic. The rate constant (k_2) and adsorption at equilibrium (q_{eq}) can be obtained from the intercept and slope, respectively. The dependence of t/q_t versus t gave a linear relation for all experimental concentrations (Fig. 6b).

The comparison of experimental adsorption capacities and the theoretical values estimated from the first- and second-order equation is presented in Table 1. The Lagergren’s model did not provide sufficient information to explain the experimental kinetic data, whereas the theoretical q_{eq} values for the adsorption of heavy metal ions on the biosorbent are very close to the experimental q_{eq} values in the case of the second-order kinetic (Table 1). This suggests that the rate-limiting step may be the chemical adsorption not the mass transport limitation. The initial adsorption rate h_0 (mg/g/min) is given in Eq. (7). The values of q_e , k_2 , h_0 and R^2 are listed in Table 1. All the R^2 values are closer to “one”, confirming the applicability of the pseudo-second-order equation. The values of the rate constants varied with the initial metal concentration. Although consistency is expected for these values when a single controlling mechanism is assumed by the model, variations do occur for natural biosorbents and are usually attributed to the heterogeneous nature of the biosorbent surface (Al-Degs et al. 2006). From Table 1, it can be observed that, with an increase in the initial metal concentration, the initial sorption rate (h_0) also increased. In accordance with the pseudo-second reaction mechanism, the overall rate of Cd(II) sorption process appears to be controlled by the chemical process, through the sharing of

electrons between the biosorbent and sorbate, or covalent forces, through the exchange of electrons between the particles involved.

An empirically found functional relationship, common to most adsorption processes, is that the uptake varies almost proportionally with $t^{0.5}$, as per the Weber–Morris plot, rather than with the contact time, “ t ”. According to this model, the plot of uptake (q) versus the square root of time should be linear if intraparticle diffusion is involved in the adsorption process, and if these lines pass through the origin, then intraparticle diffusion is the rate-controlling step. The low correlation coefficient values obtained (Table 1) for the intraparticle diffusion model indicated that adsorption does not occur in the pores of biosorbent in accordance with surface adsorption. Increasing metal ion concentration in the aqueous solutions seems to reduce the external diffusion of the adsorbate and enhances the intraparticle diffusion. If the intraparticle diffusion was involved in the adsorption process, then a plot regarding the amount of heavy metal adsorbed per unit mass of adsorbent (q_t) against square root of time ($t^{0.5}$) gave a straight line, and the particle diffusion would be the controlling step, if this line passed through the origin. The deviation of straight lines from the origin indicates that intraparticle transport is not the rate-limiting step. As seen from the Fig. 6c, the intraparticle diffusion rate equation fits well to the initial stages of the adsorption process for the tested metal ion with the P.O biomass system.

Biosorption isotherms

The successful representation of the dynamic adsorptive separation of solute from solution onto a biosorbent depends upon an appropriate description of the equilibrium separation between two phases (Febrianto et al. 2009). In order to determine the mechanism of Cd(II) biosorption onto *P. oceanica* and to evaluate the relationship between biosorption temperatures, the experimental data were tried to fit the two and three-parameter nonlinear isotherm models, i.e., Langmuir, Freundlich and Redlich–Peterson.



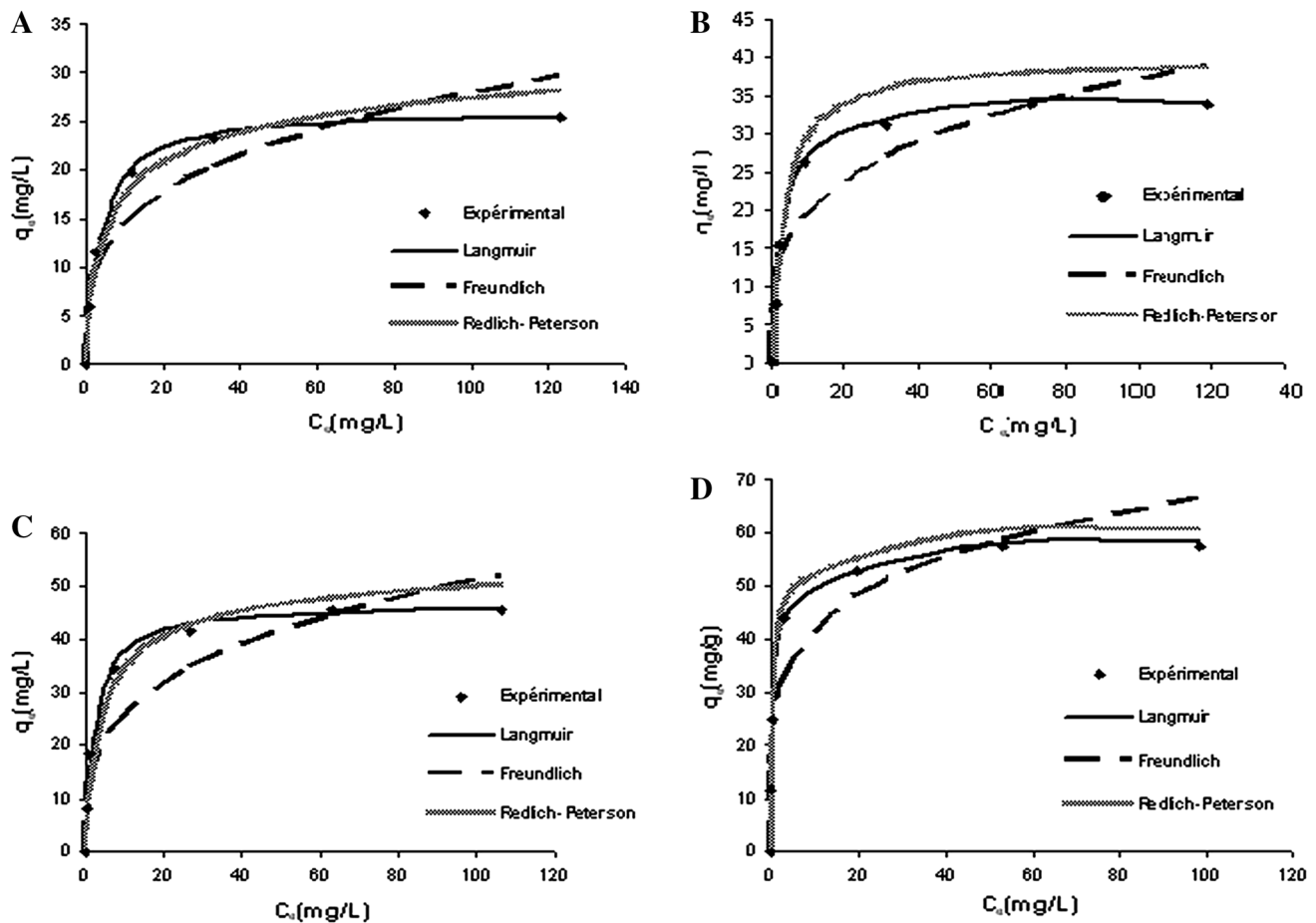


Fig. 7 Isotherms of Cd(II) adsorption by P.O as a function of temperatures (**a** 25 °C, **b** 35 °C, **c** 45 °C and **d** 55 °C) at pH 6

The Langmuir isotherm model is the often used single-component adsorption model and is shown as below (Langmuir 1918):

$$q_e = \frac{Q^0 b C_e}{1 + b C_e} \quad (9)$$

where q_e is the amount of metal ion bound per gram of dried biomass at equilibrium (mg/g) and C_e is the residual (equilibrium) metal concentration left in solution after binding (mg/L). The parameters Q^0 and b are Langmuir constants related to maximum adsorption capacity and bonding energy of adsorption, respectively, which are functions of the characteristics of the system as well as time.

The empirical Freundlich equation based on sorption on a heterogeneous surface is given below by Eq. (8) (Freundlich 1906).

$$q_e = K_F \times C_e^{\frac{1}{n}} \quad (10)$$

where K_F and n are the mono-component Freundlich constants characteristic of the system. K_F and n are indicators of biosorption capacity and biosorption intensity, respectively.

The three-parameter Redlich–Peterson model incorporated the features of the Langmuir and Freundlich isotherms into a single equation and presented a general isotherm equation as follows (Redlich and Peterson 1959).

$$q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^\beta} \quad (11)$$

where K_{RP} is the Redlich–Peterson model isotherm constant (l/g), a_{RP} the Redlich–Peterson model constant (l/mg) and β is the Redlich–Peterson model exponent. The exponent, β , lies between 0 and 1.

A model isotherm graph for the biosorption of Cd(II) at 298, 308, 318 and 328 K is shown in Fig. 7. The Langmuir adsorption constants calculated from the corresponding isotherms with the correlation coefficients are presented in Table 2. The maximum theoretical adsorption capacity of



Table 2 Langmuir, Freundlich and Redlich–Peterson constants for Cd(II) biosorption by PO

Metal ion	Temperature (K)	Langmuir			Freundlich			Redlich–Peterson			
		Q_m	b	R^2	K_F	n	R^2	K_{RP}	a_{RP}	β	R^2
Cd(II)	298	26.31	0.28	0.999	7.38	2.14	0.880	9.80	0.6	0.98	0.893
	308	34.72	0.36	0.999	10.69	2.89	0.861	11.60	0.29	1	0.879
	318	46.72	0.45	0.999	13.46	3.44	0.839	17.30	0.46	0.93	0.983
	328	58.82	0.57	0.998	26.57	4.90	0.848	25.70	0.48	0.95	0.897

Cd(II) calculated from Langmuir equation is 58.82 mg/g biosorbent at 328 K. Comparing the correlation coefficients of three isotherm models, it was observed that equilibrium data were well represented by the Langmuir isotherm model. The conformity of the biosorption data to the Langmuir isotherm could be interpreted as an indication of a homogeny adsorption process, leading to monolayer binding. The constant Q_m and b increased with increase in temperature.

The constants for the Freundlich models, K_F and $1/n$, are constants related to biosorption capacity and intensity of biosorption, respectively. The $1/n$ values are between 0 and 1, indicating that the biosorption of Cd(II) onto the PO is favorable at the studied conditions. Furthermore, the correlation coefficient values for the Freundlich model are lower than the Langmuir isotherm model.

The equilibrium biosorption data were also fitted with the Redlich–Peterson isotherm expression; however, the correlation coefficients were found to be lower than that of the Langmuir model.

Biosorption thermodynamics

Different thermodynamic parameters, such as the standard Gibbs free energy ΔG^0 , the standard enthalpy (ΔH^0) and the standard entropy (ΔS^0) for biosorption of Cd(II) onto P.O, were calculated using the following equations

$$\Delta G^0 = -RT \ln K \quad (12)$$

where K (L/g) an equilibrium constant obtained by multiplying the Langmuir constants Q^0 and b (Yao et al. 2010). R is the universal gas constant (8.314×10^{-3} kJ/mol K), and T is the absolute temperature (K).

The enthalpy (ΔH^0) and entropy (ΔS^0) parameters were estimated from the following equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (13)$$

Reciprocal of temperature ($1/T$) was plotted against $\ln K$, and a straight line was obtained (data not shown). The values of ΔH^0 and ΔS^0 calculated from the slope and intercept of the straight line are summarized in Table 3. The negative value of ΔG^0 indicates the feasibility of the

Table 3 Thermodynamic parameters of the Cd(II) biosorption on the P.O at different temperatures

T (K)	ΔG^0 (kJ/mol)	ΔS^0 (J/mol K)	ΔH^0 (kJ/mol)	R^2
298	−5.80	0.29	80.62	0.97
308	−8.70			
318	−11.60			
318	−14.50			

process and indicated the spontaneous nature of the adsorption. The values of ΔG^0 were found to increase as temperature increased, indicating more driving force and hence resulting in higher biosorption capacity. The value of ΔH^0 was positive, indicating the endothermic nature of the biosorption of Cd(II) onto P.O. In addition, the positive values of ΔS^0 show an affinity of biosorbent and the increasing randomness at the solid–solution interface during the biosorption of Cd(II) on the bark (Li et al. 2009).

Desorption and regeneration studies

In order to investigate desorption of metal ion from metal-loaded P.O, the metal-loaded biosorbent was treated with HCl, which has been reported as an efficient metal desorbent (Holan et al. 1993; Puranik and Paknikar 1997; Saeed and Iqbal 2003). Desorption studies were performed with different hydrochloric acid concentrations. From the results of this study (data not shown), with the increasing of hydrochloric acid concentration, the desorption rate also increased initially and then became almost stable. The maximum percentage recovery of Cd(II) was 96.03 % with 0.2 M HCl solution. In biosorption process, to keep the processing cost down and to open the possibility of recovering the metal(s) extracted from the liquid phase, it is desirable to regenerate the biosorbent material. In this study, 0.2 M HCl was used as a regenerating agent (or eluent). The regenerated biosorbent was reused for up to five biosorption–desorption cycles (data not shown). An efficiency of 96.03 % recovery of Cd(II) was obtained with



0.2 M HCl in the first cycle and is therefore suitable for regeneration of biosorbent. There is a gradual decrease in Cd(II) biosorption with an increase in the number of cycles. After a sequence of five cycles, the Cd(II) uptake capacity of the biosorbent was reduced from 96.03 to 89.27 %. The lost in the biosorption capacity of the biomass for metal ions was found to be <7 %. This might be due to the ignorable amount of biomass lost during the biosorption–desorption process. These results indicate that the P.O could be used repeatedly in Cd(II) biosorption studies without any detectable loss in the total biosorption capacity.

Conclusion

The experimental investigation concluded that *Posidonia Oceanica* could be used as potential biosorbent, for the removal of Cd(II) from aqueous solution. The batch study parameters: pH of solution, biomass concentration, contact time, and temperature were found to be effective on the biosorption processes. The experimental data were analyzed using Langmuir, Freundlich and Redlich–Peterson isotherm models. The equilibrium data fitted well with the Langmuir isotherm. The maximum biosorption capacity of P.O biomass for Cd(II) was found to be 58.82 mg/g. The kinetic data were analyzed using pseudo-first-order, pseudo-second-order and intraparticle diffusion models. Among the kinetic models studied, the pseudo-second-order equation was the best applicable model to describe the sorption process. The calculated thermodynamic parameters showed the feasibility, endothermic and spontaneous nature of the biosorption of Cd(II) onto P.O biomass. The reusability of the biosorbent was good after five consecutive biosorption–desorption cycles without any considerable loss in biosorption capacity based on all results; the P.O biomass can be used as alternative biosorbent for treatment of wastewaters containing Cd(II) ions.

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