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Removal of cadmium from aqueous solution by *Posidonia oceanica* (L.) leaf sheaths fibres using discontinuous stirring tank reactor

F. Kaouah*, T. Berrama, L. Brahmi, S. Boumaza, Z. Bendjama

Laboratoire des Sciences de Génie des Procédés Industriels, Faculté de Génie des Procédés et Génie Mécanique, Université des Sciences et de la Technologie Houari Boumediene USTHB, BP 32, EL Allia, Bab Ezzouar, Algérie
Email: faridakaouah@yahoo.fr

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ABSTRACT

In the current research, the leaf sheath fibres of *Posidonia oceanica* (L.) were used as a low–cost, available and renewable biological adsorbent for the removal of cadmium from aqueous solutions. Experiments were carried out in a batch reactor. The effect of physical–chemical parameters such as contact time, adsorbent dosage, initial pH and initial Cd^{2+} concentration were investigated. Two adsorption isotherm models namely the Langmuir and Freundlich were used to analyse the equilibrium data. The data are very well represented by the Langmuir isotherm, which confirm the monolayer coverage. The kinetic modelling study has shown that the experimental data were found to follow the pseudo-second-order model, suggesting a chemisorption process. The result suggests that leaf sheath fibres of *P. oceanica* (L.) have high potentiality to be used as an effective and economical biosorbent for Cd^{2+} removal.

Keywords: Cd (II); *Posidonia oceanica*; Biosorption; Isotherms; Kinetics models

1. Introduction

The tremendous increase in the use of heavy metals over the past few decades has inevitably resulted in an increase flux of metallic substances in the aquatic environment. Cd, Cr, Cu, Hg, Ni, Pb and Zn are the most common metals discharged into water streams from large industrial sectors [1]. The metallic substances are extremely stable and persistent environmental contaminants since they cannot be degraded or destroyed, and therefore tend to accumulate in the soils, seawater, freshwater and sediments. Among the metals, cadmium belongs to the group of hazardous metals and has attracted a great attention of researches. It is extensively used in various industrial applications, such as electroplating, Ni–Cd batteries, smelting, alloys manufacturing, and pigments, plastic, mining and refining processes. Cadmium has been classified as a human carcinogen and teratogen impacting lungs, kidneys, liver and reproductive organs [2,3]. The harmful effects also include a number of acute and chronic disorders, such as renal damage, emphysema, hypertension and testicular atrophy. It is, therefore, essential to develop efficient

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*Corresponding author.

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procedures for its removal from the wastewater before disposal. Several methods have been purposed, which include precipitation, flotation, ion exchange, membrane-related process, electrochemical reduction and biological process [4,5]. However, applications of such technologies are restricted because of technical or economic constraints [6,7]. The adsorption was studied and emerged as one of the promising techniques due to its simplicity of design, easy operation and insensitivity to toxic substances [8]. The activated carbon is a well-known adsorbent and has proven to be useful for the removal of heavy metals. Nevertheless, the application of activated carbon for wastewater treatment is not feasible due to its high price and cost associated with the regeneration as a result of high degree of losses in real process [9]. Therefore, this last decade, there has been an increasing interest to find cheap and easily provided natural adsorbents. Several natural materials such bacteria [10], alga [11,12], yeast [13], fungi [14], sub-products of agriculture [15] and industry, biopolymers [16] have been tested to remove heavy metals from water. These renewable resources can be used for metal binding through a number of different reactions including ion exchange, electrostatic attraction and complexation [17]. Marine biomass represents an important resource for adsorption processes. Marine plants such as *Posidonia oceanica* have shown its effectiveness in removing organic pollutants [18–20] and heavy metals [21,22]. *P. oceanica* is very abundant in the Mediterranean Sea and is a highly fibrous material made of cellulose and hemicellulose (about 60–75%) and lignin (about 25–30%) [23].

The main aim this study was to investigate the effectiveness of a marine lignocellulosic material, *P. oceanica* leaf sheaths, for cadmium adsorption. The effect of various parameters such as pH, biosorbent dosage, contact time and initial Cd^{2+} concentration was investigated. To determine the correlation between the isotherm models and experimental data, Langmuir and Freundlich equations have been applied. Thermodynamic and kinetic parameters were calculated to determine the adsorption mechanism.

2. Materials and methods

2.1. Preparation of the sorbent

Fibrous *P. oceanica* leaf sheaths were collected from the west coast of Algiers and the biosorbent was prepared from the leaves. After being collected, the samples were washed with tap water and then with distilled water to remove dirty particles like sand and salt absorbed at the surface of the biomass. The washing process was continued until the conductivity value became stable. The biomass was cut in strips of 1–2 cm in length and then dried in an oven at 60°C for 24 h, until a constant weight is reached. The dried biomass was stored in a desiccator for further use. The dried leaves were crushed and sieved. Only the sample of 200 μm particle size was used in the adsorption experiments.

2.2. Preparation of the metal solution

The Cd^{2+} solution was prepared by dissolving ($Cd(NO_3)_2 \cdot 4H_2O$) in distilled water. The initial concentration varies from 75 to 200 $mg\,L^{-1}$. The initial pH of the solution was adjusted by using HNO_3 or NaOH solutions.

2.3. Metal biosorption experiments

The biosorption experiments were carried out in batch mode at a room temperature. A given mass of biosorbent was added to the Cd^{2+} solution and the mixture was stirred during a given time. The aliquots were withdrawn at regular time intervals and filtered through a filter paper (Double Boxing rings 102). Cd^{2+} analysis was realized by atomic absorption spectrophotometer (Perkin–Elmer, A 800) at a wavelength of 228.8 nm, a slit of 0.5 and one flame of the air–C_2H_2 type. The percentage of equilibrium Cd^{2+} biosorption uptake, q_e (mg/g), was calculated using the following relationships:

$$\%\,\text{Removal} = \frac{100(C_0 - C_e)}{C_0} \tag{1}$$

$$q_e = \frac{(C_0 - C_e)v}{m} \tag{2}$$

where C_0 ($mg\,L^{-1}$) is the initial cadmium concentration in liquid phase, C_e ($mg\,L^{-1}$) denotes the cadmium concentration in liquid phase at equilibrium, V (L) represents the total volume of the cadmium solution, and m (g) is the mass of sorbent.

2.4. Biosorption isotherm modelling

Adsorption isotherms are important to bring insights on the adsorption mechanism of a solute on adsorbent surface in order to optimize the design of a specific adsorption process. The equilibrium data obtained for Cd^{2+} removal using *P. oceanica* were analysed within the context of two common adsorption *models*; the Langmuir and Freundlich adsorption isotherms. They are simple, give a good description of experimental behaviour over a large range of operating conditions and re-characterized by a limited number of adjustable parameters [24].

2.4.1. Langmuir isotherm

The Langmuir isotherm [25] is based on monolayer coverage of adsorbent surface by the adsorbate at specific homogeneous sites within the adsorbent; it is represented by:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{3}$$

where q_e is the equilibrium concentration of the adsorbate on the adsorbent (mg g^{-1}) and C_e the equilibrium concentration of the solute in the liquid phase expressed as mg L^{-1}; q_m (mg g^{-1}) and K_L (L mg^{-1}) are the Langmuir equation constants, representing the maximum adsorption capacity and adsorption energy parameter, respectively. Eq. (3) can be converted to linear form linearized in equation (Eq. (4)), and the plot of C_e/q_e vs. C_e gives a straight line with $1/q_m$ as slope and $1/q_m K_L$ as intercept:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{4}$$

A further analysis of the Langmuir equation can be made using a dimensionless equilibrium parameter, the separation factor R_L:

$$R_L = \frac{1}{1 + K_L C_0} \tag{5}$$

For a favourable adsorption, the value of R_L should lie between 0 and 1; $R_L > 1$ indicates an unfavourable adsorption, $R_L = 1$ represents the linear adsorption, whereas $R_L = 0$ translates into the irreversible adsorption [26].

2.4.2. Freundlich isotherm

The isotherm model developed by Freundlich [27] is based on multilayer adsorption of adsorbate onto a heterogeneous surface with a non-uniform distribution of heat of adsorption:

$$q_e = K_F C_e^{1/n} \tag{6}$$

where q_e is the equilibrium concentration of the adsorbate on the adsorbent in mg g^{-1} and C_e the equilibrium concentration of the solute in the liquid phase (mg L^{-1}); K_F and n are the Freundlich equation parameters. The linear form of the Freundlich equation is given by

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{7}$$

A plot of log q_e vs. log C_e of Eq. (7) should result in a straight line whose slope and intercept give the values of n and K_F, respectively. The Freundlich isotherm is derived by assuming a heterogeneous surface.

2.5. Biosorption kinetics model equations

In order to investigate the Cd^{2+} biosorption mechanism on *P. oceanica* and the potential rate-controlling steps such as chemical reaction and mass transfer, kinetic models have been used to fit the experimental data [28]. Many models have been proposed to describe the reaction order based on solution concentration. The models based on the adsorbent capacity have also been presented, such as the Lagergren's equation and Ho's second-order expression. The pseudo-first-order and pseudo-second-order models fit the data very well [29].

2.5.1. Pseudo-first-order model

The pseudo-first-order rate of the *Lagergren* based on the solid capacity [30] is widely used for assigning the adsorption rate of adsorbate from a liquid phase:

$$\frac{dq}{dt} = K_1 (q_e - q) \tag{8}$$

where q_e (mg g^{-1}) and q (mg g^{-1}) are the adsorption capacity at equilibrium and time (t), respectively, and K_1 (min^{-1}) is the rate constant of the pseudo-first-order adsorption reaction. By integration and applying boundary conditions as $q = 0$ at $t = 0$ and $q = q_e$ at $t = t_e$, Eq. (8) becomes

$$\log(q_e - q) = \log q_e - \frac{K_1 t}{2.303} \tag{9}$$

The value of the rate constant K_1 is determined from the linear plot log $(q_e - q)$ against t.

2.5.2. Pseudo-second-order model

The pseudo-second-order kinetic expression was developed by Ho and McKay [31] to describe the adsorption of metal ions onto adsorbents. The rate expression is given by:

$$\left(\frac{\mathrm{d}q}{qt}\right) = K_2(q_\mathrm{e} - q)^2 \tag{10}$$

where K_2 ($\mathrm{g\,mg^{-1}\,min^{-1}}$) is the rate constant for the pseudo-second-order adsorption reaction.

The integrated second-order rate equation, at boundary conditions $q = 0$ at $t = 0$ and $q = q_\mathrm{e}$ at $t = t_\mathrm{e}$, becomes

$$\frac{t}{q} = \frac{1}{K_2 q_\mathrm{e}^2} + \frac{t}{q_\mathrm{e}} \tag{11}$$

The constants q_e and K_2 are calculated from the linear plot of Eq. (11). The initial adsorption rate is obtained as q/t, when t approaches zero:

$$h = K_2 q_\mathrm{e}^2 \tag{12}$$

where h ($\mathrm{mg\,g^{-1}\,min^{-1}}$) is the initial adsorption rate.

3. Results and discussions

3.1. Properties of the biosorbent

The works of Ncibi et al. [32] and Wahab [33] on the characterization of *P. oceanica* by analytical techniques (elemental analysis, SEM, FTIR) show that carbon and oxygen are the main components of the biomass. Furthermore, *P. oceanica* as a vegetal biomaterial contains mainly lignin and cellulose, and can be viewed as natural ion-exchange material that primarily contains weak acidic and basic groups on the surface [34,35]. In addition, the textural characterization shows that *P. oceanica* has a typical compact lignocellulosic fibrous structure and is intrinsically not porous. Indeed, like all lignocellulosic-based fibers, the *Posidonia* ones are formed by several holocellulosic microfibers, which are linked together via lignin. The FTIR analysis displays a number of absorption peaks such as carboxylic, carbonyl, hydroxyl and phenolic groups, indicating the complex nature of examined biomass.

3.2. Effect of operating parameters

3.2.1. Effect of contact time

To study the rate of Cd^{2+} removal by sorption on *P. oceanica*, the time contact effect is investigated. Fig. 1 shows the percentage of Cd^{2+} removal for different values of the initial Cd^{2+} concentration ($75–200\,\mathrm{mg\,L^{-1}}$), at pH 7. For the first 60 min, when Cd^{2+} concentration increases, the Cd^{2+} removal decreases from 93.58 to 20.45%, and reaches the values of 98.06 and 24.93% at 120 min. The rate of Cd^{2+} removal using *P. oceanica* is increased rapidly till 60 min. A further increase in the contact time has a negligible effect on the adsorption rate. The variation in the extent of biosorption may be due to the fact that initially all sites on the surface of sorbent are vacant and the solute concentration gradient is relatively high. Consequently, the extent of Cd^{2+} species uptake decreases with the increase of the contact time which is dependent on the decrease in the number of vacant sites on the surface of the biosorbent. Generally, when the biosorption involves a surface reaction process, the initial biosorption is rapid. Then, the biosorption is attenuated, as the available sites gradually decrease, which is consistent with studies reported before [36,37]. The data obtained from effect of contact time are further used to determine the kinetics of Cd (II) biosorption.

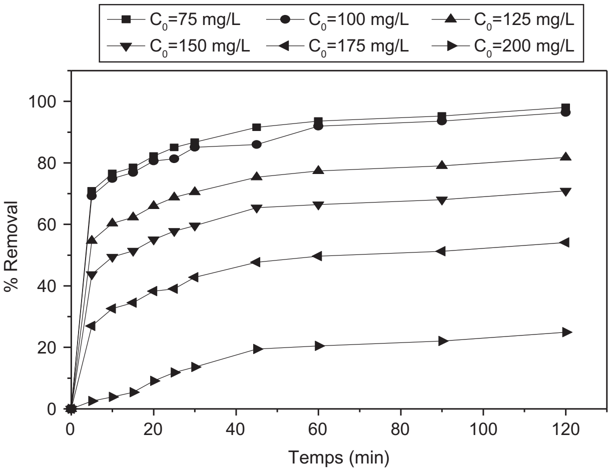

Fig. 1. Effect of contact time on the cadmium removal by biomass.

3.2.2. Effect of pH on cadmium removal

The pH is an important parameter for the biosorption since it may affect the speciation of the metal, the stability of the biomass and the chemical state of its reactive groups.

At basic pHs, most heavy metals readily precipitate as hydroxides. Considering the solubility product constant (K_s) of $Cd(OH)_2$, ranging between 0.5 and 5.0×10^{-14} (M^3) [38], $Cd(OH)_2$ precipitation may occur at pH values higher than 8. The pH threshold for precipitation depends on both the K_s value and the Cd^{2+} concentration (C_0). For instance, calculations lead to the following pH values for Cd $(OH)_2$ precipitation: 8.4 for $K_s = 5 \times 10^{-15}$ and $C_0 = 200\,mg\,L^{-1}$, and 9.2 for $K_s = 5 \times 10^{-14}$ (M^3) and $C_0 = 75\,mg\,L^{-1}$.

To avoid any influence of Cd^{2+} precipitation on the sorption performance, experiments were carried out by varying pH from 3 to 8 (Fig. 2). The percentage of Cd^{2+} removal is minimum (79.70%) at pH 3 and increases up to the pH value of 7, then remains nearly constant (91.94%) when pH ranges between 7 and 8. Based on these results, following experiments were conducted at pH 7. The dependence of Cd^{2+} uptake on pH is related to both the functional groups present on the biomass surface and the Cd^{2+} chemistry in solution. At low pH, the surface ligands are closely associated with the hydronium ions (H_3O^+) and restrict the approach of Cd^{2+} as a result of the repulsive force [39,40]. Furthermore, the pH dependence on the Cd^{2+} uptake can also be justified by the association–dissociation of certain functional groups of the biomass, such as the carboxyl and hydroxyl groups. Most of the carboxylic groups are not dissociated at low pH and cannot bind Cd^{2+}, although they take part in complexation reactions [41]. Similar results have already been reported in other works which have shown low adsorption capacity at acidic pH, but it increases at higher pH values [26,42].

3.2.3. Effect of biosorbent dosage

Biosorbent dosage is an important parameter because it determines the biosorbent capacity for a given initial concentration of the adsorbate. The effect of biosorbent dose over the range 0.25–2 $g\,L^{-1}$ onto the metal biosorption is shown in Fig. 3. The percentage of cadmium removal increases from 28.80 to 91.94%. When adsorbent dose increases, more surface area is available; this implies an increase in the number of active sites for binding of metal ions. These observations are in agreement with others reported in the literature for the biosorption of Cd^{2+} by different biological materials [43].

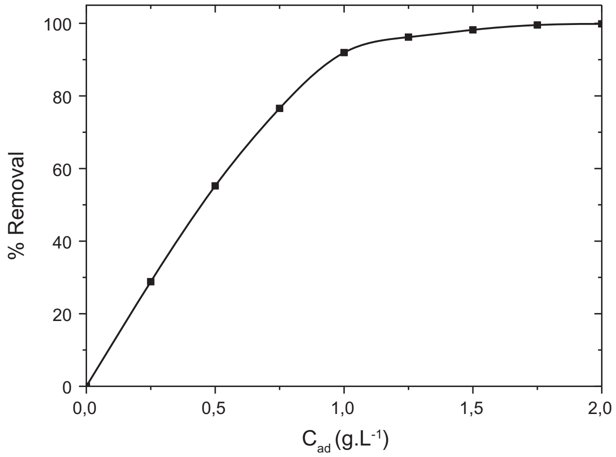

Fig. 3. Effect of the biosorbent dose on the Cd^{2+} removal by biomass.

3.2.4. Effect of initial cadmium concentration

The biosorption is significantly influenced by the initial Cd^{2+} concentration in aqueous solutions. The sorption of Cd^{2+} by *P. oceanica* is investigated at various initial concentrations (75, 100, 125, 150, 175 and 200 $mg\,L^{-1}$) using 1.0 g of biosorbent dose; the pH initial of solution is 7. Fig. 4 shows that when increasing the Cd^{2+} concentration, the percentage of cadmium removal decreases from 98.06 to 24.93%. At the low

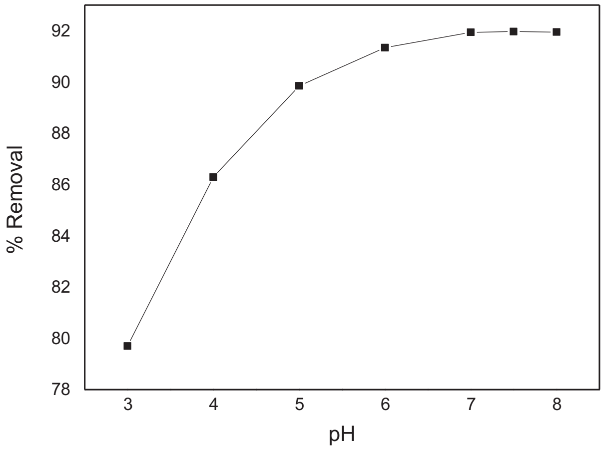

Fig. 2. Effect of pH on cadmium the removal by biomass.

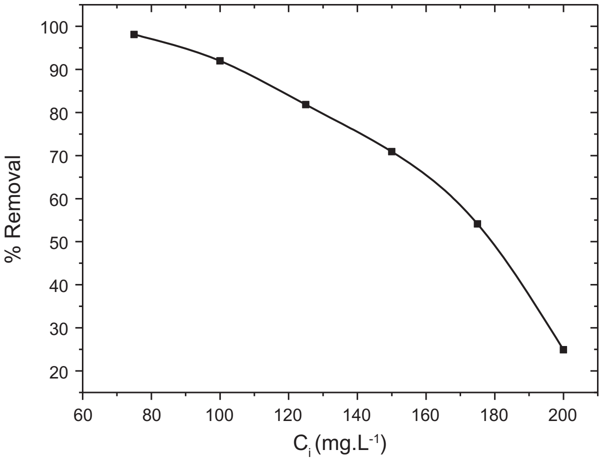

Fig. 4. Effect of the initial Cd^{2+} concentration on the removal on the biomass.

initial concentrations, the surface area, or in other words the availability of adsorption sites, is relatively high, and therefore Cd^{2+} is easily adsorbed. By contrast, at high concentrations, the total number of available adsorption sites is limited, thus resulting in a decrease in the percentage of Cd^{2+} removal. Similar results were reported by other researchers [44,45].

3.3. Biosorption isotherm

The equilibrium studies were carried out under the optimal conditions i.e. pH 7, a biosorbent dose of $1\,g\,L^{-1}$ at 25°C, and by changing the initial Cd^{2+} concentrations. The equilibrium experimental data are analysed using the Freundlich and Langmuir isotherm models (Eqs. (4) and (7)). The isotherms are illustrated in Fig. 5 and the various parameters are given in Table 1. All the plots show a straight line, indicating that the Cd^{2+} biosorption follows the both isotherms. The comparison of the correlation coefficients indicates that the Langmuir isotherm fits the results more accurately ($R^2 = 0.999$) than the Freundlich one ($R^2 = 0.9663$); this confirms the monolayer formation during the biosorption, that the molecules have equal activation energy and the sorbate–sorbate interaction is negligible. The Langmuir constant, q_m, which measures the monolayer adsorption capacity of *P. oceanica* and Langmuir constant K_L, which denotes adsorption energy, was given in Table 1. The dimensionless parameter, R_L, was found in the range (0.0112–0.0294) which confirms favourable Cd^{2+} biosorption on *P. oceanica* ($0 < R_L < 1$).

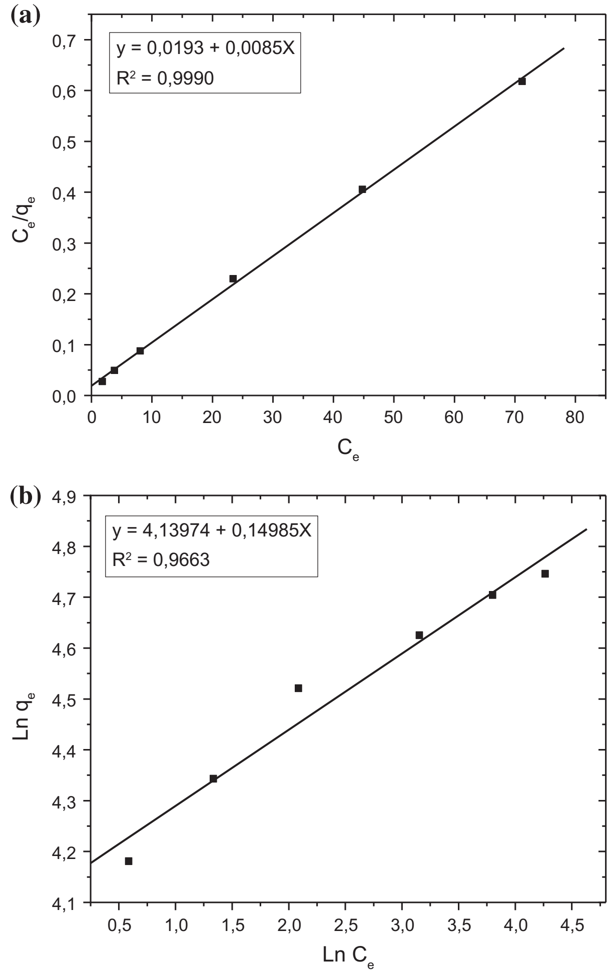

Fig. 5. Langmuir (a) and Freundlich (b) biosorption isotherms of Cd (II) ions on *P. oceanica*.

A comparative study of the maximum Cd^{2+} uptake capacity of *P. oceanica* is carried out with other reported sorbents. It is to be noted that the maximum amount of Cd^{2+} uptake by various sorbents varies as a function of the experimental conditions. The temperature and pH have an important effect on the amount of Cd^{2+} uptake per unit sorbent [46]. Therefore, for a direct and meaningful comparison, the maximum Cd^{2+} amount biosorbed on *P. oceanica* is compared with reported sorbents under different conditions (Table 2). It is observed that much except olive stone [47], *P. oceanica*, is by far the better sorbent. The differences of metal uptake are due to the properties of each biosorbent material such as structure, functional groups and surface area. The availability and cost effectiveness of *P. oceanica* are further advantages, which make it an attractive biosorbent for the treatment of the effluents containing cadmium.

3.4. Biosorption thermodynamics

The temperature dependence of the biosorption process is associated with several thermodynamic parameters and the question to be settled at this level is to know whether the process is spontaneous or not. The free energy is related to the equilibrium constant according to Eq. (13):

$$\Delta G^0 = -RTLnK_D \tag{13}$$

Table 1
Langmuir and Freundlich constants for cadmium biosorption on biomass

Model Langmuir	q_m (mg g^{-1})	K_L (L mg^{-1})	R^2
Constants	117.647	0.440	0.9990
Model Freundlich	K_F (mg1–1/n g^{-1} L1/n)	n	R^2
Constants	62.794	6,665	0.9663

Table 2
Sorption capacity of different low-cost sorbents for the uptake of Cd (II) from its aqueous solution

Adsorbent	$q_{\max}$ (mg g^{-1})	pH	T (°C)	Reference
Microalga *Scenedesmus obliquus*	68.60	6.0	30	[48]
Brevundimonas sp	49.01	6.0	30	[49]
Bacillus jeotgali	53.50	7.5	30	[50]
Oedogonium sp.	88.20	5.0	25	[51]
Spirulina platensis	98.04	6.0	26	[52]
Olive stone	128.20	4.0	25	[47]
Pseudomonas veronii	54.00	7.5	32	[53]
Rhizopus cohnii	40.50	4.5	25	[54]
Mung bean husk	35.41	5.0	25	[55]
Maize corncob	105.60	6.0	30	[56]
Posidonia oceanica	117.65	7.0	20	This work

The relation between ΔG^0, the entropy change (ΔS^0) and the enthalpy of adsorption is given by the relation 14:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{14}$$

Combining the two equations, one gets:

$$\mathrm{Ln}K_{\mathrm{D}} = -\frac{\Delta G^{\circ}}{RT} = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{R}\frac{1}{T} \tag{15}$$

where T is the absolute temperature (K), R is the universal gas constant and K_{D} (=$q_{\mathrm{e}}/C_{\mathrm{e}}$) is the single point or linear sorption distribution coefficient. By plotting Ln K_{D} vs. $1/T$, the values of ΔH^0 and ΔS^0 are deduced from the slope and intercept, respectively (Fig. 6). The parameters values of ΔG^0, ΔH^0 and ΔS^0 are listed in Table 3.

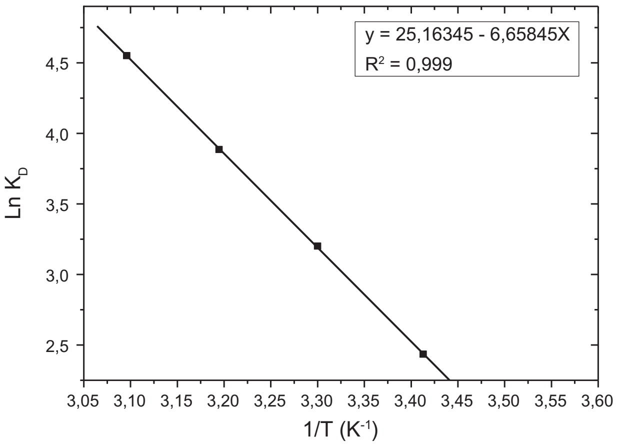

Fig. 6. Plot of Ln K_{D} vs. $1/T$ for the estimation of thermodynamic parameters.

The negative values of ΔG^0 indicate that the Cd^{2+} biosorption onto *P. oceanica* is a spontaneous process, while the positive value of ΔH^0 over the range 20–50°C shows that the process is endothermic in nature and an increase in T causes an increase of the constant K_D. The positive value of ΔS^0 reflects the affinity of *P. oceanica* for Cd^{2+} with an increasing randomness at the solid/liquid interface. Similar results have been obtained by Srivastava et al. for Cd^{2+} biosorption on bagasse fly ash and rice husk ash [57].

3.5. Biosorption kinetic study

The linear forms of the pseudo-first-order model and the pseudo-second order model are shown in Fig. 7(a) and (b), respectively. The kinetic parameters including the first-order rate constant k_1, second-order rate constant k_2, the equilibrium adsorption capacity $q_{\mathrm{e,cal}}$ and experimental equilibrium adsorption capacity $q_{\mathrm{e,exp}}$ for Cd^{2+} and the coefficients R^2 are gathered in Table 4. The pseudo-first-order model gives correlation coefficients (R^2 relatively low, lying between 0.840 and 0.986). In addition, the difference between $q_{\mathrm{e,exp}}$ and $q_{\mathrm{e,cal}}$ is very high. On the other hand, the $q_{\mathrm{e,cal}}$ using the pseudo-second-order model is in good agreement with the experimental $q_{\mathrm{e,exp}}$ values. The

Table 3
Thermodynamic parameters for biosorption of Cd (II) onto *P. oceanica*

T (°K)	ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})	ΔG^0 (kJ mol^{-1})
293	55.396	209.346	−5.942
303			−8.036
313			−10.129
323			−12.222

Table 4
Kinetic rate constants for pseudo-first-order and pseudo-second-order models at various temperatures

T (℃)	$q_{e,exp}$ (mg g^{-1})	Pseudo first order rate constants			Pseudo second order rate constants		
		k_1 (min^{-1})	q_e (cal) (mg g^{-1})	R^2	K_2 (min^{-1})	q_e (cal) (mg g^{-1})	R^2
20	91.94	3.85×10^{-2}	88.45	0.9552	8.07×10^{-3}	91.18	0.997
30	96.08	3.56×10^{-2}	95.17	0.9862	7.12×10^{-3}	97.16	0.996
40	97.98	4.81×10^{-2}	74.65	0.8402	6.33×10^{-3}	98.40	0.999
50	98.95	10.59×10^{-2}	90.45	0.9142	5.40×10^{-3}	99.14	0.999

coefficients (R^2) for all temperatures are very high, greater than 0.996. Thus, the Cd^{2+} biosorption onto *P. oceanica* is more appropriate to describe the pseudo-second-order model. Hence, the biosorption is mainly governed by chemical process involving cations sharing or exchange between biosorbent and Cd^{2+} ions in the solution [58,59].

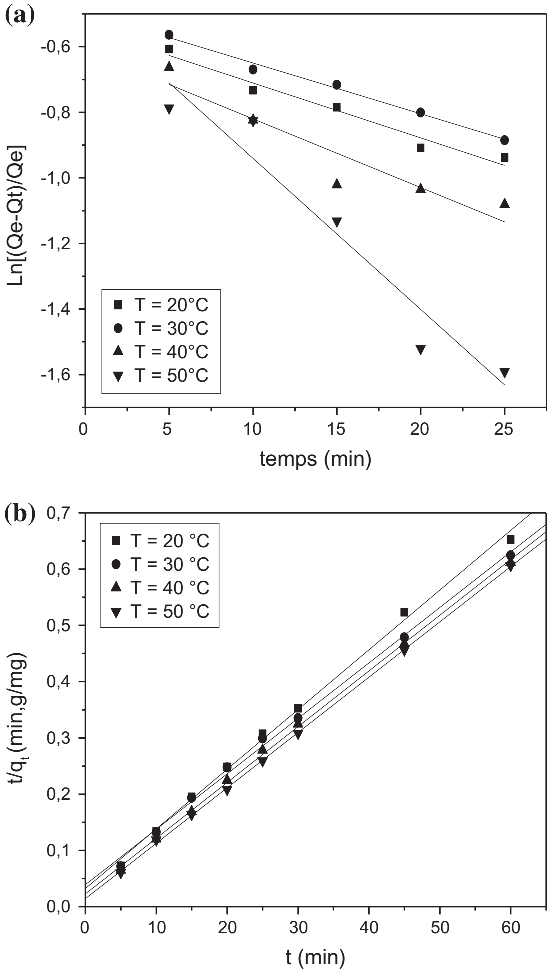

Fig. 7. (a) First-order and (b) second-order kinetic models for biosorption Cd^{2+} onto *P. oceanica*.

3.6. FTIR analysis

The FTIR spectra were useful in the range 500–4,000 cm^{-1} to identify the characteristic functional groups responsible for the Cd^{2+} biosorption [60–63]. The spectra of *P. oceanica* before and after the biosorption were examined to determine the possible interactions between the functional groups and Cd^{2+} (Fig. 8). The spectrum (Fig. 8(a)) shows the presence of several functional groups, indicating the complex nature of *P. oceanica*. The broad and strong band at 3,411 cm^{-1} suggests the presence of –OH and $–NH_2$ groups [64]. The peak at 2,923 cm^{-1} can be attributed to –CH stretching vibrations while the peak appearing at 1,738 cm^{-1} arises from C=O stretching in amide groups [64,65]. The peak at 1,044 cm^{-1} corresponds to C–O stretching vibration of alcohols and carboxylic acids [66]. After Cd^{2+} biosorption (Fig. 8(b)), the spectrum was not drastically modified. Indeed, some peaks, such as those corresponding to –OH and $–NH_2$, registered a slight horizontal shift. This change in the peaks suggests that these functional groups are involved in the Cd^{2+} biosorption.

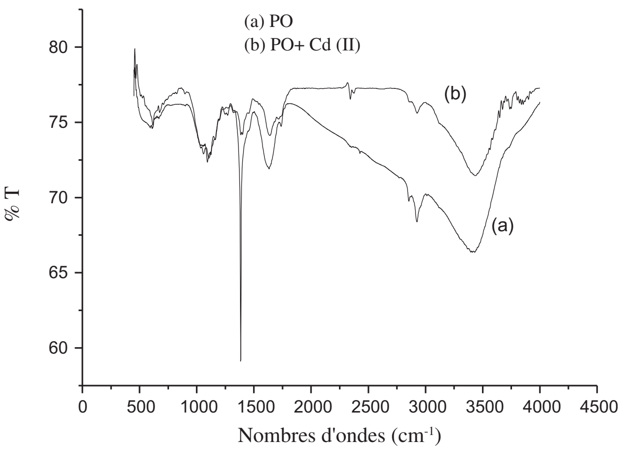

Fig. 8. FTIR spectra of *P. oceanica* (a) before biosorption (b) after biosorption of Cd (II).

4. Conclusion

In this work, we examined the biosorption ability of *P. oceanica* (L.) leaf sheaths fibres for the cadmium adsorption. It has been shown that the highest percentage removal of cadmium was found at neutral pH. The biosorption equilibrium uptake was enhanced by increasing the biomass dose up $1\,\mathrm{g\,L^{-1}}$ for an initial Cd^{2+} concentration of $100\,\mathrm{mg\,L^{-1}}$. The kinetic rate constants of the pseudo-first-order and pseudo-second-order equations were determined; the last model was found to be more appropriate to satisfactorily describe the biosorption phenomenon. The biosorption modelling parameters for the Freundlich and Langmuir isotherms were determined on the basis of the correlation coefficients. The equilibrium data fit well with both the models: Freundlich and Langmuir. The results indicate that *P. oceanica* (L.) leaf sheaths fibres may be used as an inexpensive, effective and easy as biosorbent without any treatment for the removal of cadmium from aqueous solutions.

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