



Kinetic and equilibrium studies of biosorption of M(II) (M = Cu, Pb, Ni, Zn and Cd) onto seaweed *Posidonia oceanica* fibers

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Abstract

This work reports the application of *Posidonia oceanica* for the elimination of heavy metals M(II) (M = Zn, Cd, Ni, Cu and Pb) by biosorption in batch system. The effect of the contact time, initial M concentration, pH and temperature was considered. The kinetic and equilibrium models for the M-biosorption were tested namely the pseudo-first-order, pseudo-second-order and Elovich kinetic models. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms models have also been used to fit equilibrium adsorption data. The adsorption kinetics follow a pseudo-second-order model for all studied systems, and the equilibrium data are suitably fitted by the above models. The amount of adsorbed metals by biosorption is 48.33, 43.9, 41.02, 37.90 and 30.22 mg/g for Pb(II), Cu(II), Ni(II), Zn(II) and Cd(II), respectively. The thermodynamic parameters suggested that the metal biosorption is spontaneous with an endothermic nature.

Keywords Biosorption · Heavy metals · *Posidonia oceanica* · Isotherm · Kinetic

Introduction

The environmental pollution by heavy metals is a serious threat and a complex problem that has been and is still a focus of attention throughout the world since they are non-biodegradable and exist in all the food chain. Many organic, inorganic and biological substances have been reported as water contaminants (Gupta et al. 2002; Saravanan et al. 2013), whose toxicity has been observed to exceed the permissible limit (Gupta and Saleh 2013). The metals are among the major pollutants in surface and underground waters, and both industrial and municipal wastewaters contain metal ions which are hazardous to the human health (Krishnani et al. 2008; Gupta et al. 2013). Waste streams containing toxic metals are often encountered in the industry and can be the source of metals in the aquatic environment. Copper is widely used in various fields such as plating, mining and electroplating, refining of oil, etc.... (Demirbas et al. 2009). Cadmium is employed in batteries, paints and plastics

(Low et al. 2000), whereas zinc is used in acid galvanizing plants (Tunali and Akar 2006). The industry also uses nickel in various products (detergents, metal-based jewelry, steel and many other metal products) (Venkateswarlu et al. 2015). All these metals are not biodegradable and have negative effects on the flora and fauna (Rozaini et al. 2010). They cause chronic bronchitis and reduced lung function (cancer of the lungs) (Ahmaruzzaman and Gupta 2011).

The Environmental Protection Agency (EPA) has included these metals on the list of priority pollutants (Volesky 2001). However, their removal from water is a very difficult task due to the high cost of treatment methods. Conventional techniques of removing metals from wastewater are high cost with some limitations. They include chemical precipitation, mainly hydroxides and sulfides, membrane filtration (reverse osmosis, nano-filtration), electrolytic reduction, solvent extraction, electrocoagulation, ions exchange and adsorption (Huang and Wu 1977; Calugaru et al. 2016; Juang and Shiau 2000; Gupta and Ali 2004; Heidmann and Calmano 2008; Qiu and Zheng 2009; Bessbousse et al. 2008).

The elimination of metals by biosorption remains an attractive alternative and is promising because of its potential application in the environmental protection. The biosorption uses biological materials such as raw rice husk (Mohan and Sreelakshmi 2008), olive pomace (Pagnanelli

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et al. 2005), wood bark (Palma et al. 2003), peat (Ma and Tobin 2003), lignin (Wu et al. 2008) and agro-industrial wastes (Johnson et al. 2002; Nguyen et al. 2013). The main advantage of the biosorption is the low cost, high yield, decrease in both chemical and biological sludge, lack of nutrient requirements, biosorbent regeneration and uptake of metal recovery.

Marine biomass including chitosan, chitin, crab shell and algae represents an important resource for the biosorption; the biomass considered in this study is *Posidonia oceanica*. The endemic herbarium *P. oceanica* occupies a central position in the ecology of the Mediterranean Sea, its importance lies in its extension, high productivity and stability, and its grasslands are functional as a spawning area, hunting area or permanent habitat for different plants and animals. In addition, it possesses chelating properties toward heavy metals which makes it promising in biosorption. This ability to uptake toxic metals is attributed to the existence of alginate and to the porosity of the cell wall which allows small ionic species (Boudouesque et al. 2012).

The aim of this research is the evaluation of the performance and efficiency of *P. oceanica* as a new biosorbent for the M(II) elimination (M = Ni, Cd, Cu, Pb and Zn). The influence of physical parameters affecting the biosorption such as pH, contact time, M(II) concentration, temperature and biosorbent dose was studied. The adsorption is studied in terms of pseudo-first- and pseudo-second-order kinetics, and different isotherm models are applied to experimental data to obtain information on the interaction metal/*P. oceanica*.

Materials and methods

Adsorbent preparation and characterization

Posidonia oceanica was collected along the shoreline of the western region of Algiers (Tipaza). This harvest site was chosen because of the high abundance of submarine herbariums of this phanerogam which is therefore conducive to the formation of balls resulting from the fraying of dead leaves. The balls were washed and dried at 40 °C for 48 h. This temperature allows desiccation of the material without affecting its structural and functional characteristics. Dried waste was reduced to a fine powder in a centrifugal ball mill for 45 min (400 rpm) and sieved to get a size fraction less than 160 µm.

The BET specific surface area was determined by adsorption–desorption isotherms of N₂ at 77 K using a Micromeritics ASAP 2010 apparatus. The FTIR spectroscopy was used to give a qualitative analysis of the main chemical groups present on the biomass and responsible of the adsorption. The translucent samples disks were prepared by mixing

0.1 g of biomass/g of KBr; the spectra were recorded with a PerkinElmer Spectrum Tow. The point of zero charge (pzc) was determined by simple electrolyte addition method; 0.1 g of *P. oceanica* fibers was immersed into 50 mL of KNO₃ (0.05 M) at different pH solutions and shaken at constant speed for 24 h. After decantation, the difference between the initial and final pHs was plotted against the initial pH (Mahmood et al. 2011). The same suspension was used to determine the zeta potential, measured with Mastersizer 3600, Malvern. Scanning electron microscopy (SEM, Jeol-JSM-6360 LV) provides a view of the morphological structure of the biosorbent.

Adsorbate

Stock M(II) solutions (1000 mg/L) with which the experiments were conducted were prepared by dissolving nitrate salts: Ni(NO₃)₂, Zn(NO₃)₂, Pb(NO₃)₂, Cd(NO₃)₂ and Cu(NO₃)₂ in distilled water; other concentrations (30–250 mg/L) were prepared by dilution. HCl and NaOH solutions (0.1 M) were used for the pH adjustment.

Biosorption experiment

The experimental tests were conducted in batch mode by varying pH from 2 to 8, temperatures (20, 30 and 40 °C), *P. oceanica* dose (0.05–0.5 mg) and M(II) concentrations (30–250 mg/L). For each experiment, an accurate quantity of *P. oceanica* was added to 50 mL of M(II) solutions in conical flasks (100 mL), shaken in a thermostatic shaker (300 rpm). The suspensions were filtered with Whatman 41 filter paper. The M(II) quantities before and after equilibrium were analyzed by atomic adsorption spectrometry (PerkinElmer 3030), and the adsorbed amount (q_e) was calculated from the formula.

$$q_e = \frac{V}{m} \cdot (C_0 - C_e) \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations (mg/L), m the amount of adsorbent (g), and V the volume of solution (L). The removal efficiency percentage of metal ($E\%$) was calculated as follows:

$$E(\%) = 100 \cdot (C_0 - C_e) / C_0 \quad (2)$$

Biosorption kinetics and equilibrium

Kinetics

The kinetics were studied in conical flasks; 0.1 mg of biosorbent was contacted with 50 mL of M(II) solution (100 mg/L); the concentration was determined at regular time intervals. The adsorption kinetic data were fitted by

the pseudo-first-order, pseudo-second-order and Elovich models.

The pseudo-first order is given by Belhamdi et al. (2016):

$$\ln(q_e - q_t) = \ln q_e - tk_1 \tag{3}$$

where q_e and q_t (mg g⁻¹) are the amounts of M(II) adsorbed at equilibrium and time t (min), respectively and k_1 the equilibrium rate constant (min⁻¹). q_e and k_1 are calculated from the slope and intercept of the plot $\ln(q_e - q_t)$ versus t .

The linear form of pseudo-second-order equation is expressed by the relation (Belhamdi et al. 2016; Ghaedi et al. 2015):

$$\frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \frac{1}{q_e} t \tag{4}$$

where k_2 (g mg⁻¹ min⁻¹) is the equilibrium rate constant. q_e and k_2 are calculated from the plot $\frac{t}{q_t}$ versus t .

The Elovich model was applied satisfactorily to chemisorption processes (Hannachi 2012):

$$q_t = \left(\frac{1}{b}\right) \ln(ab) + \frac{1}{b} \ln t \tag{5}$$

where a (mg g⁻¹ min⁻¹) is the initial biosorption rate and b (g mg⁻¹) the desorption constant related to the extent of surface coverage and activation energy; they are obtained from the linear plot of q_t versus $\ln t$.

Equilibrium

Equilibrium studies were carried out at 20, 30 and 40 °C. The biomass (0.1 mg) was contacted with M(II) solutions in the concentrations range (30–250 mg/L) at pH 6, for 80 min.

The Freundlich, Langmuir, Temkin and Dubinin–Radushkevich (D–R) models were used for describing the solid–liquid adsorption system.

The Freundlich model assumes a heterogeneous surface with adsorption sites of different energies (Freundlich 1907; Mittal et al. 2010):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{6}$$

where K_F is a constant related to the bonding energy, $1/n$ the heterogeneity factor and n (g L⁻¹) measures the deviation from linearity of adsorption. The equilibrium constants are determined from the plot $\log q_e$ versus $\log C_e$. The regression coefficient (R^2) measures the fit goodness of the experimental data to the isotherm models.

The Langmuir adsorption model considers specific homogeneous sites on the surface, when a site is occupied by a molecule; no further adsorption can take place and is expressed by Ahmad et al. (2018) and Mohammadi et al. (2011):

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{1}{q_{\max}} C_e \tag{7}$$

where K_L is a constant related to the energy of adsorption and q_{\max} the maximum adsorption capacity (mg g⁻¹). They are calculated from the linear plot of C_e/q_e versus C_e .

The Temkin model assumes that the adsorption energy decreases linearly with the surface coverage due to adsorbent–adsorbate interactions (Dada et al. 2012); its linear form is given by:

$$q_e = RT \ln K_T + \frac{RT}{b_r} \ln C_e \tag{8}$$

where b_r is a constant related to heat of sorption (J mol⁻¹) and K_T the isotherm constant (L g⁻¹); these constants were obtained from the plot of q_e versus $\ln C_e$.

The D–R model is semiempirical, and the adsorption follows a pore-filling mechanism. It assumes that the adsorption has a multilayer character and involves Van Der Waals forces; it is applicable for physical adsorption, and the linear form is expressed by Ahmad et al. (2018):

$$\ln q_e = \ln q_m - \beta \epsilon^2 \tag{9}$$

where q_m is the D–R constant (mg g⁻¹), β the constant related to free energy and ϵ the Polanyi potential which is defined as:

$$\epsilon = RT \ln(1 + (1/C_e)). \tag{10}$$

Results and discussion

Characterization of biosorbent

The FTIR spectra of *P. oceanica* (data not shown) show a peak at 3333 cm⁻¹ due to (–OH) or amine groups (–NH), while the band at 2903 cm⁻¹ represents the stretching of –CH groups. The bands 1407 and 772 cm⁻¹ are attributed to –CH bending, and those observed at 1720 and 1672 cm⁻¹ are assigned to C=O stretching groups. The peak at 1600 cm⁻¹ could be attributed to N–H bending, while those at 1407 and 1027 cm⁻¹ are assigned to –CN stretching. Similar results are reported on the copper removal by *P. oceanica* (Hannachi et al. 2014).

A relationship exists between the zeta potential and biosorption capacity; the latter varies with pH and helps to understand the behavior of suspended biomaterials in solution (Feng et al. 2009).

The zeta potential was determined under different pHs (Fig. 1), and the potential of the biomass decreases from –5.9 to –18.9 mV with increasing pH (6–11). The negative charges on the biosorbent surface could be explained by the alkalization of the solution. Indeed, according to

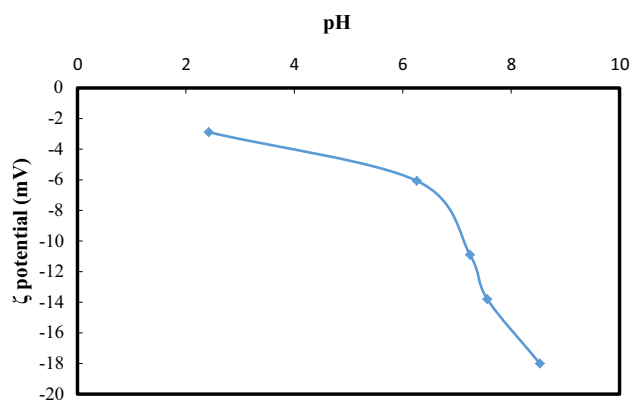


Fig. 1 Zeta potential of *Posidonia oceanica* at various pH values

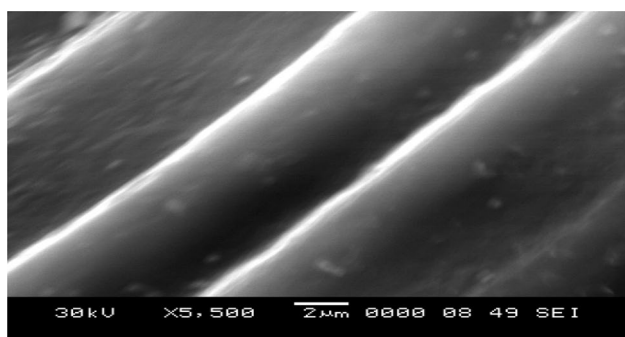


Fig. 2 SEM images of *Posidonia oceanica* fibers

Table 1 The physicochemical characteristics of the *Posidonia oceanica*

Parameter	Value
Specific surface area ($\text{m}^2 \text{g}^{-1}$)	4.35
Average pore diameter (μm)	160
pHpzc	7.9

Kam and Gregory (2001), basic pH induces the hydrolysis and loss of cationic groups and reduces the protonation of surface groups of the algae. The ($-\text{OH}$) groups deprotonate at high pH, it convert to O^- , and such transformation generates negative charges on the surface (Park and Regalbuto 1995).

The *P. oceanica* fibers, characterized by SEM analysis (Fig. 2), have lignocellulosic fibrous structure with cylindrical fibers shape. Furrows are observed on the outer surface of the biomass, due to the dehydration of the cell wall. This morphology plays an important role in the adsorption and precipitation of M(II) on the external surface; other physicochemical are gathered in Table 1.

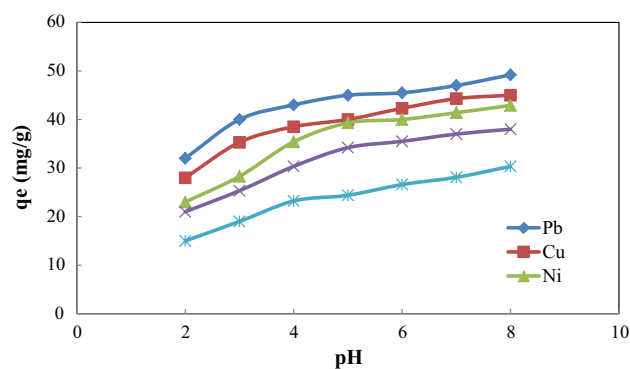


Fig. 3 Effect of pH on the heavy metal biosorption onto *Posidonia oceanica* fibers

Effect of pH

The pH has a great influence on the M(II) removal by adsorption, because it directly affects the surface charge and the nature of ionic species of the adsorbates. In this context, the pH effect was studied in the range (2–8). The removal capacity of M(II) increases with increasing pH (Fig. 3); the minimal adsorption at pH 2 is due to the high concentration of H^+ ions which compete with the M(II) adsorption and are preferentially fixed by carboxyl, hydroxyl and amine groups present on the *P. oceanica* surface (Pérez-Marín et al. 2007). When the pH increases, the biomass surface becomes negatively charged, leading to increased M(II) uptake and reaches equilibrium at pH 6. The retention capacity of M(II) decreases above pH 6 because of the apparition of insoluble M(OH)_2 , and all hydroxides have a solubility product smaller than 10^{-15} . Adsorption and precipitation are the two mechanisms responsible for the M(II) elimination (Wang and Qin 2005).

Effect of biosorbent dose

The effect of biosorbent dose was carried out over the range (50–500 mg); these quantities were added to 50 mL of M(II) solution (100 mg/L), and the M(II) concentration was determined at equilibrium. The M(II) uptakes were found to increase linearly with increasing the dose (Fig. 4); they reach 97, 98, 88, 85 and 70% for Pb(II) , Cu(II) , Ni(II) , Cd(II) and Zn(II) , respectively, for a biomass dose of 250 mg. The availability of biosorption sites depends upon the biosorbent dose. The stability of M(II) uptake with increases in the biosorbent dose is due to the split in the flux between the M(II) concentration in the solution and the sorbent surface (Wang and Qin 2005).

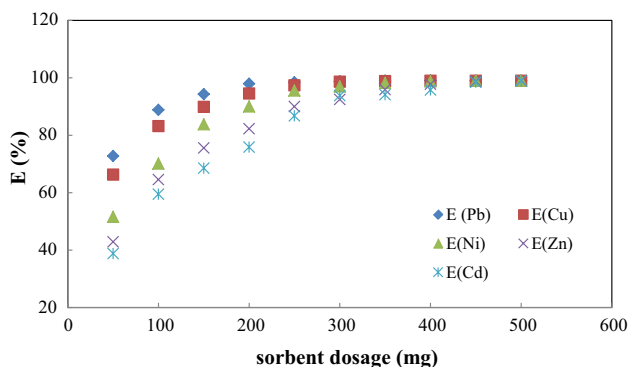


Fig. 4 Effect of the sorbent dose on the % removal of Zn(II), Ni(II), Cu(II), Pb(II) and Cd(II) by *Posidonia oceanica*

Effect of the contact time

In order to control the effect of the contact time on the metal biosorption and to estimate the time sufficient to achieve equilibrium, the experiments were carried out at pH ~ 6, a biomass dose of 0.1 g, an initial M(II) concentration of 100 mg/L and a temperature of 25 °C. The concentration of M(II) in solution was determined at regular time intervals

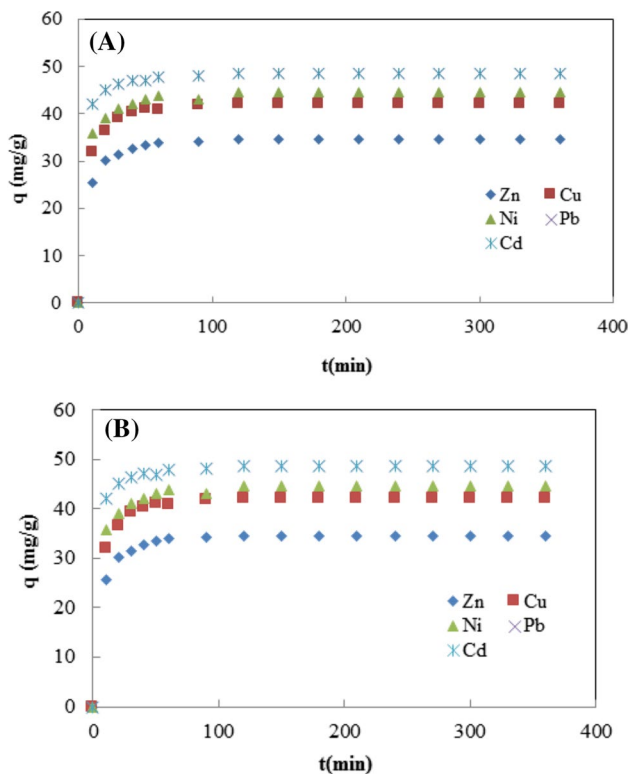


Fig. 5 a Effect of contact time on the % metal removal and b on the uptake of Zn (II), Ni (II), Cu (II), Pb(II) and Cd (II) by *Posidonia oceanica*

(Fig. 5). The biosorption increases over time and reaches equilibrium after 80 min. The removal efficiency of the biosorbent increases rapidly in the initial stage (0–30 min) because of the abundant active binding sites on the biomass (Madala et al. 2017) and becomes less efficient during the second stage (30–80 min) to reach a saturation; this can be explained by the interaction with the functional groups located on the biosorbent surface and intercellular

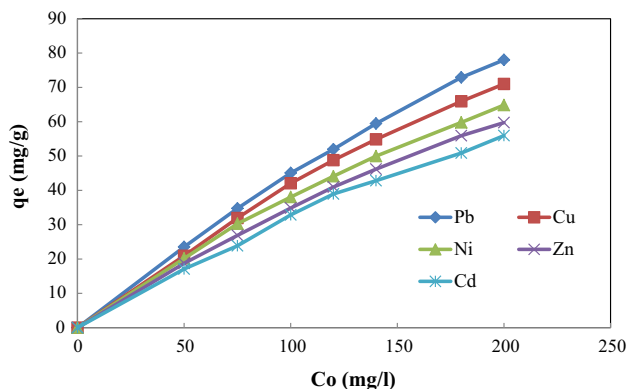


Fig. 6 Effect of the initial concentration of heavy metals on the uptake of Zn(II), Ni(II), Cu(II), Cd(II) and Pb(II) by *Posidonia oceanica*

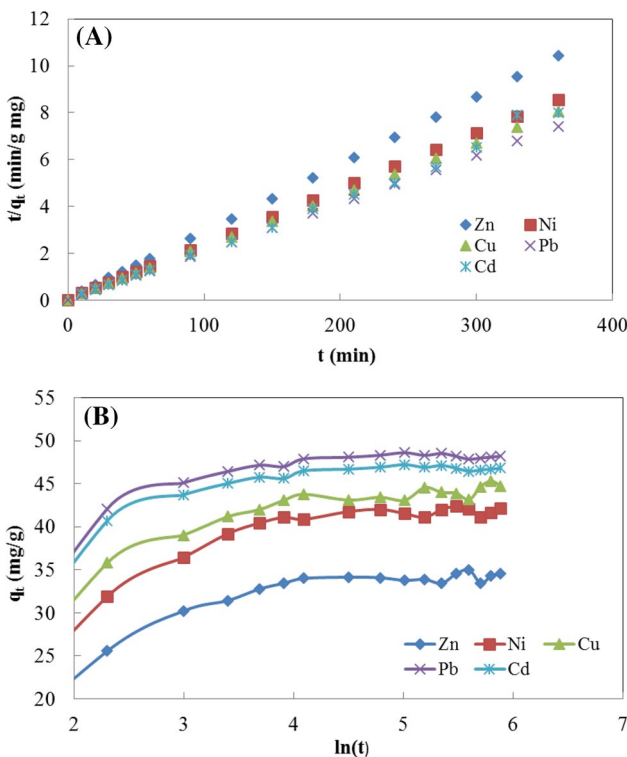


Fig. 7 a Plots of pseudo-second-order kinetics of Zn(II), Ni(II), Cu(II) and Pb(II) by *Posidonia oceanica* and b plots of Elovich kinetics of the heavy metals adsorption

accumulation (Liu et al. 2006). Based on these results, a shaking time of 80 min was suitable for further biosorption experiments.

Effect of the initial concentration of heavy metals

The effect of the M(II) initial concentration on the biosorption by *P. oceanica* is investigated by varying the initial M(II) concentration in solution from 30 to 250 mg/L, maintaining the other parameters constant. The results show that the retention capacity of metal by the biomass increases with raising the M(II) concentration in solution (Fig. 6). This due to the interaction M(II)/biosorbent which provides the driving force to overcome the resistance to the mass transfer of M(II) ions between the solution and solid phase. In addition, the enhanced biosorption with the M(II) concentration is due to an increase in the electrostatic interactions (physical adsorption versus covalent interactions) (Arshadi et al. 2014). The M(II) absorption can be attributed to various mechanisms of ion exchange and adsorption processes (Bektaş and Kara 2004; Buasri et al. 2007).

Table 2 Kinetic parameters for the biosorption of heavy metals by *Posidonia oceanica* fibers

Heavy metal ions	Pseudo-first-order model		
	R^2	k_1 (min ⁻¹)	q_1 (mg/g)
Cu(II)	0.659	0.026	6.49
Ni (II)	0.664	0.031	6.44
Pb(II)	0.592	0.027	5.78
Zn(II)	0.655	0.029	6.00
Cd(II)	0.659	0.023	5.42
Heavy metal ions	Pseudo-second-order model		
	R^2	$k_2 \times 10^{-3}$ (mg/ (g.min))	q_2 (mg/g)
Cu(II)	0.999	0.304	45.45
Ni (II)	0.999	0.201	43.47
Pb(II)	0.999	0.48	50
Zn(II)	0.999	0.496	34.48
Cd(II)	0.999	0.473	49.32
Heavy metal ions	Elovich model		
	R^2	a (mg/ (g.min))	b (mg/g)
Cu(II)	0.707	11.85	0.172
Ni (II)	0.717	11.42	0.179
Pb(II)	0.636	13.25	0.166
Zn(II)	0.707	11.85	0.172
Cd(II)	0.689	12.25	0.171

Kinetics studies

The biosorption kinetics of M(II) on *P. oceanica* were undertaken to establish the adsorption equilibrium time (Fig. 7) and kinetic parameters (Table 2). The validity of each model was verified by the fitness of the correlation coefficient (R^2). The $q_{e(cal)}$ values calculated from the pseudo-first-order model differ from the experimental ones. By contrast, in the pseudo-second-order model, the calculated $q_{e(cal)}$ values are very close to $q_{e(exp)}$, and the R^2 values converge to 1, indicating the validity of the pseudo-second order (Ncibi et al. 2009). For the Elovich model, the plots are not linear with bad coefficients R^2 , suggesting that the biosorption follows rather the pseudo-second-order kinetic model based on the assumption that the rate-determining step is a chemisorption, involving valence forces through sharing or exchange of electrons between adsorbent/adsorbate (Ghodbane and Hamdaoui 2008).

Table 3 Freundlich, Langmuir, Temkin and Dubinin–Radushkevich constants for Zn(II), Ni(II), Cu(II), Pb(II) and Cd(II) into *Posidonia oceanica*

Freundlich	K_f (mg/g)	n	R^2
Pb(II)	7.69	2.51	0.970
Cd(II)	3.33	1.61	0.941
Cu(II)	5.89	1.39	0.933
Zn(II)	4.05	1.68	0.982
Ni(II)	5.13	1.86	0.988
Langmuir	q_{max} (mg/g)	K_L (L/mg)	R^2
Pb(II)	100	11.8	0.995
Cd(II)	100	71.9	0.960
Cu(II)	111.11	28.66	0.991
Zn(II)	111.11	62.22	0.993
Ni(II)	100	38.88	0.991
Temkin	b_1 (J/mol)	K_T (L/g)10 ⁻³	R^2
Pb(II)	124.96	4.31	0.990
Cd(II)	113.99	46.2	0.979
Cu(II)	103.65	27.1	0.994
Zn(II)	107.14	46.2	0.992
Ni(II)	108.64	35.33	0.991
D–R	q_m (mg/g)	B	R^2
Pb(II)	11.86	- 4.508	0.935
Cd(II)	11.45	- 24.42	0.960
Cu(II)	12.09	- 12.05	0.991
Zn(II)	11.57	- 18.85	0.954
Ni(II)	11.71	- 13.92	0.961

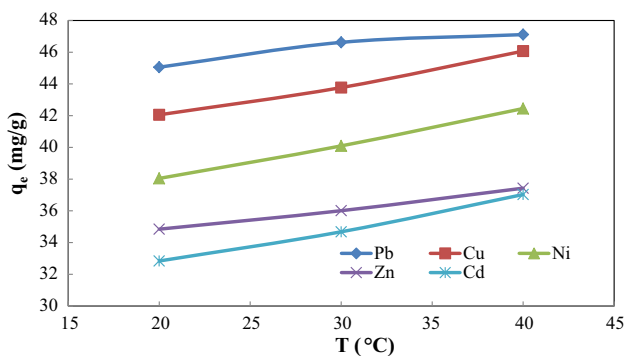


Fig. 8 Effect of temperature on the uptake of Zn(II), Ni(II), Cu(II), Cd(II) and Pb(II) by *Posidonia oceanica*

Isotherm studies

The isotherms data provide information on the capacity of the adsorbent or the amount required to remove a unit mass of pollutant under the operating conditions. In this study, the equilibrium data of M(II) adsorbed onto *P. oceanica* were fitted by the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) isotherms, and the corresponding parameters are given in Table 3. On the basis of correlation coefficients R^2 , it is concluded that the M(II) biosorption is better fitted to the Langmuir and Temkin models. This suggests that the biosorption of M(II) on the surface of *P. oceanica* occurs on homogeneous binding sites with equivalent adsorption energies and monolayer coverage (Ncibi et al. 2009).

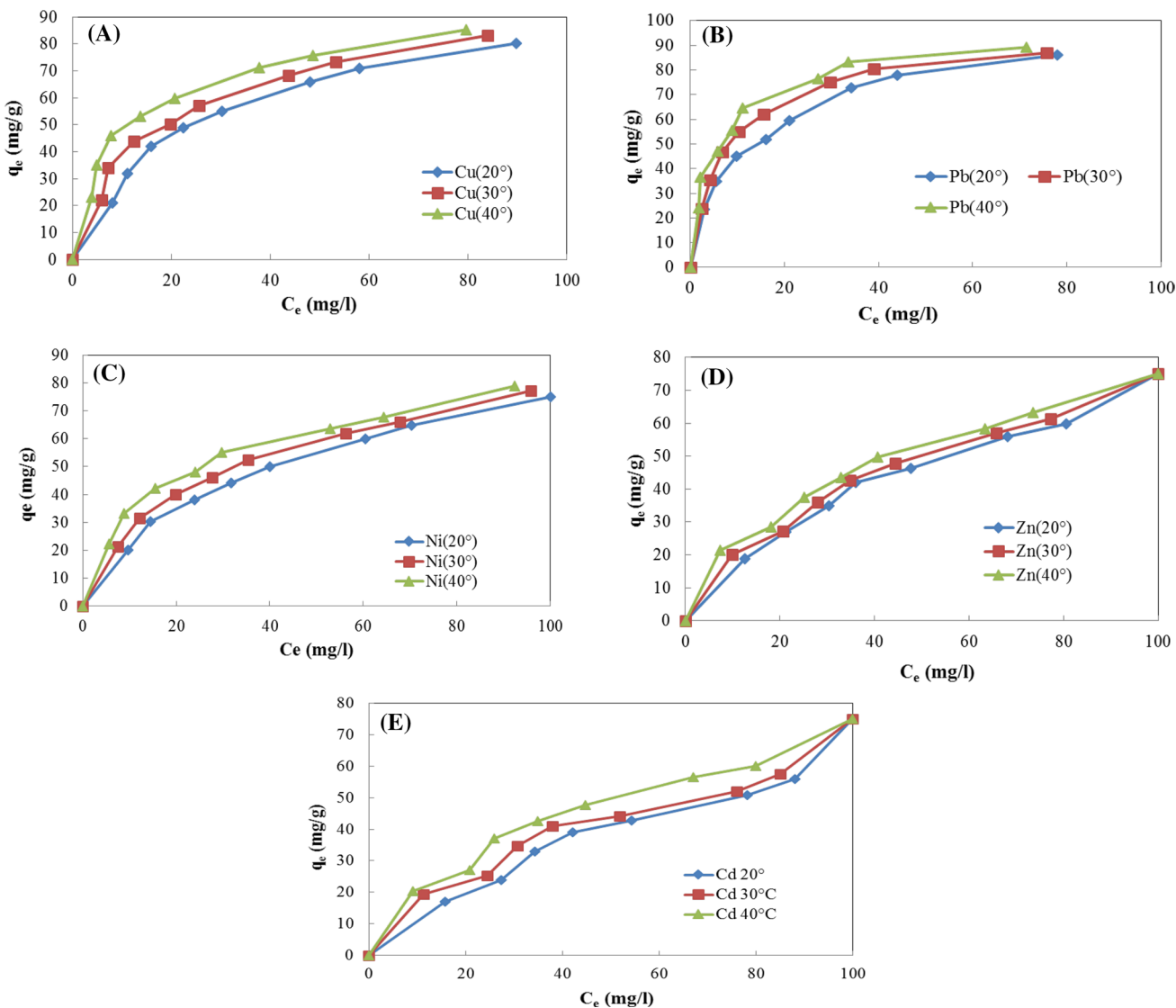


Fig. 9 Effect of the temperature on the adsorption of five heavy metals by *Posidonia oceanica*

Thermodynamic studies

To study the effect of thermal on the M(II) biosorption by *P. oceanica*, the temperature was varied from 20 to 40 °C using constant parameters at equilibrium. The test was performed below 40 °C to avoid evaporation of the solution. The M(II) biosorption at different temperatures (Figs. 8 and 9) shows that the uptake capacity increases with augmenting temperature and confirms the endothermic nature of retention of M(II) by *Posidonia oceanica* (Ghodbane and Hamdaoui 2008). The metal uptake is favored at higher temperature, since it activates the metal ions for enhancing the biosorption at the coordinating sites of the mineral (Rajamohan et al. 2014). The amounts of M(II) adsorbed versus the final concentration for different temperatures show that the biosorption creases with raising temperatures, confirming the endothermic nature and could be explained by availability of more active sites (Gupta and Rastogi 2008).

The thermodynamic parameters (ΔG° , ΔH° and ΔS°) were determined from the following equation:

$$\Delta G^\circ = -RT \ln K_C \quad (11)$$

where R is the universal gas constant. The thermodynamic equilibrium constant K_C is determined by:

$$K_C = \frac{C_{Ae}}{C_e} \quad (12)$$

where C_{Ae} and C_e are the equilibrium concentrations of M(II) (mg/L) on adsorbent and in solution, respectively (Krika et al. 2016). The thermal effect on thermodynamic constant is determined by Eq. (13)

$$\ln(K_C) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (13)$$

where ΔH° and ΔS° are calculated from the slope and intercept of the linear plot, of $\ln K$ versus $1/T$. The free energy is given by Eq. (14):

$$\Delta G^\circ = \Delta H^\circ - S^\circ \quad (14)$$

The free energy (ΔG°) is negative and increases with temperature (Table 4), indicating that the best biosorption is obtained at higher temperature while the positive enthalpy ΔH° suggests an endothermic adsorption. A similar behavior was reported by Ahmaruzzaman and Gupta (2011) for the adsorption of heavy metals by rice husk ash, and the positive entropy ΔS° confirms the increased randomness at the solid–liquid interface. The necessity of heat to remove the M(II) ions from the solution makes the biosorption process endothermic (Al-Sou'od 2012).

Table 4 The thermodynamic parameters for the biosorption of heavy metals onto *Posidonia oceanica*

Heavy metal ions	ΔH° (kJ/mol)	ΔS° (kJ/mol K)	T (K)	ΔG° (kJ/mol)
Pb(II)	321.99	1.36	293	−76.49
			303	−90.09
			313	−103.69
Cu(II)	436.65	1.68	293	−55.59
			303	−72.39
			313	−88.83
Ni(II)	312.98	1.20	293	−38.62
			303	−50.62
			313	−62.62
Zn(II)	142.18	0.58	293	−27.76
			303	−33.56
			313	−39.36
Cd(II)	219.95	0.82	293	−20.31
			303	−28.51
			313	−36.71

Comparison with literature

The maximum biosorption capacity of *P. oceanica* for the removal of Pb(II), Cu(II), Ni(II), Zn(II) and Cd(II) was compared with that of other biosorbents, and the maximum biosorption capacities (q_{max}) are gathered in Table 5. It can be noteworthy that the *P. oceanica* biomass has a considerable potential for the removal of metals compared to those of the literature. The reduction of the above metals on semi-conducting oxides upon solar light is our next objective; preliminary results were satisfactory and will be reported very soon.

Conclusion

The present work showed that *P. oceanica* fibers, a low cost biosorbent available abundantly at Algerian coasts, has an important capacity to remove the metals Zn(II), Ni(II), Cd(II), Cu(II) and Pb(II) from the aqueous medium. Based on the experimental results, it was concluded that:

1. The retention rate increases with increasing the contact time until reaching equilibrium after 80 min;
2. The maximum adsorption was determined in the pH range (6–8), close to the natural medium. The amount of adsorbed metals follows the sequence: 48.33, 43.9, 41.02, 37.90 and 30.22 mg/g, for Pb(II), Cu(II), Ni(II), Zn(II) and Cd(II), respectively;

Table 5 Comparison of maximum biosorption capacities of heavy metals on various biosorbents

Biosorbent	Biosorption capacity q_{\max} (mg/g)	References
Pb(II)		
<i>Posidonia oceanica</i>	48.33	This study
Rice husk ash	12.63	Feng et al. (2004)
<i>Aspergillus niger</i>	34.69	Dursun (2006)
Tea waste	65.00	Amarasinghe and Williams (2007)
<i>Amanita rubescens</i>	38.40	Sarı and Tuzen (2009)
Cu(II)		
<i>Posidonia oceanica</i>	43.90	This study
Raw <i>S. cerevisiae</i>	8.25	Guler et al. (2014)
<i>Aspergillus niger</i>	33.11	Dursun (2006)
Spent grain	10.47	Lu and Gibb (2008)
Green alga <i>Cladophora fascicularis</i>	47.02	Deng et al. (2007)
Crab shell particles	163.90	Vijayaraghavan et al. (2006)
Ni(II)		
<i>Posidonia oceanica</i>	41.02	This study
Rice husk ash	4.71	Srivastava et al. (2009)
Raw <i>S. cerevisiae</i>	21.39	Guler and Sarioglu (2014)
<i>Yarrowia lipolytica</i>	112.35	Shinde et al. (2012)
Cone biomass of <i>T. orientalis</i>	12.42	Malkoc (2006)
Zn(II)		
<i>Posidonia oceanica</i>	37.90	This study
Rice husk ash	5.88	Srivastava et al. (2008)
Palm tree leaves	14.60	Abu Al-Rub (2006)
<i>Penicillium simplicissimum</i>	65.60	Fan et al. (2008)
<i>Botrytis cinerea</i>	12.98	Tunali and Akar (2006)
Cd(II)		
<i>Posidonia oceanica</i>	30.22	This study
Rice husk ash	3.04	Srivastava et al. (2009)
Coconut copra meal	4.92	Ho and Ofomaja (2006)
<i>Amanita rubescens</i>	27.30	Sarı and Tuzen (2009)
<i>Lactarius scrobiculatus</i>	53.10	Anayurt et al. (2009)

- The elimination capacity of M(II) is influenced by the biosorbent dose which peaks at 2 g/L, allowing the elimination of 97, 98, 88, 85 and 70% of Pb(II), Cu(II), Ni(II), Cd(II) and Zn(II), respectively;
- The equilibrium data fit well with the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich models;
- From thermodynamic studies, the free energy (ΔG°) is negative and increases with temperature. This indicated that better biosorption is obtained at higher temperature, thus reflecting the feasibility and spontaneous nature of the process. The positive enthalpy ΔH° suggested an endothermic biosorption.

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