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Biosorption potential of the mediterranean plant (*Posidonia oceanica*) for the removal of Cu^{2+} ions from aqueous media : Equilibrium, kinetic, thermodynamic and mechanism analysis

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Abstract−The biosorption characteristics of copper(II) ions using *Posidonia oceanica* biomass were investigated. Experimental parameters affecting the biosorption process such as pH level, contact time, biosorbent dosage and temperature were studied. The equilibrium data were applied to the Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models. The Langmuir model fitted very well the equilibrium data, and the maximum uptake of Cu(II) by *Posidonia oceanica* was found to be 76.92 mg/g. The mean free energy E (10.78 kJ/mol) from the D-R isotherm indicated a chemical ion-exchange mechanism. Kinetic results showed that the pseudo-second-order kinetic model was well fitted to the experimental data. Thermodynamic parameters depicted the exothermic nature of biosorption and the process was feasible and spontaneous. The results of FTIR (Fourier-transform infrared spectroscopy) revealed that carboxyl, amine, and hydroxyl groups on the biomass surface were involved in the biosorption of Cu(II) ions.

Keywords: *Posidonia oceanica*, Biosorption, Thermodynamic Studies, Kinetic, FTIR, Desorption

INTRODUCTION

Heavy metal releases to the environment have been increasing continuously as a result of industrial activities and technological developments, posing a significant threat to the environment and public health because of their toxicity, accumulation in the food chain and persistence in nature. Copper(II), one of the heavy metals, is widely used in many industries including metal cleaning and plating, paper board, printed circuit board, wood pulp, fertilizer, paints and pigments, etc. [1]. Minute amount of copper is essential for human, animals, and microorganisms. However, excessive copper can be detrimental to the environment. The permissible limit for Cu^{2+} in drinking water, as described by the World Health Organization (WHO), is 1.5 mg/L [2]. For instance, for human it will cause intestinal distress, kidney damage, and anemia [3], and prolonged inhalation of copper containing fumes has been linked to increase in lung cancer. In view of the toxicity and to meet regulatory safe discharge standards, it is essential to remove copper from wastewaters/effluents before it is released into the environment.

The conventional processes used to remove copper ions from the contaminated environments include solvent extraction, chemical precipitation, ion exchange, activated carbon adsorption, chelation, reverse osmosis, coagulation-precipitation, electrochemical operation and filtration. However, those physicochemical technologies are expensive and environmentally disruptive, requiring input of external chemical additives or energy, as well as generating concentrated toxic sludge or other wastes that must be disposed [4,5]. These disadvantages are especially apparent at low metal concentrations often encountered in wastewaters. Therefore, efficient and environmentally compatible means need to be developed to remove or detoxify heavy metals in an economical way.

Biosorption, often referred to as passive uptake and physicochemical binding of chemical species or ions to biomass or biopolymers, has been suggested as a potential alternative to the existing physicochemical technologies for the detoxification and the recovery of toxic and valuable metals from wastewaters [6,7]. The biosorption process offers the advantages of low operating costs, reduced amount of chemical and/or biological sludge to be disposed off, and high efficiency in decontinuating effluents with dilute metal ion content.

Among the different biological substrates studied, lignocellulosic biomass (*Posidonia oceanica*) has received much attention due to the cost saving, low sensitivity to environmental and impurity factors, the possible contaminant recovery from the biomaterial. *P. oceanica* is an endemic marine magnoliophyta found in the Mediterranean sea. During autumn and winter, the bers of this plant accumulate in considerable quantities, reaching a thickness of 1-2 m or more on the most Mediterranean beaches [8]. These bers are not appreciated by the swimmers, because of the smell, but especially because they assimilate this accumulation into pollution. Huge quantities of these wastes are either transported (or possibly buried) in landlls, or piled up in adjacent areas to beaches or even re-immersed in the sea. Our purpose is to optimize the management of this important waste as a biosorbent [9].

This paper presents the study of biosorption characteristics of powdered Posidonia oceanica biomass for removing Cu(II) from aqueous solutions in batch system. The binding capacity of powdered Posidonia oceanica for Cu(II) was shown as a function of initial pH, contact time, temperature and biomass dosage in this study. The biosorption equilibrium was expressed by the Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) isotherms. Kinetic and ther-

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modynamic parameters were also calculated to describe the biosorption mechanism of Cu(II) *P. oceanica* biomass. The probable mechanism involved in the copper biosorption was explored by Fourier transform infrared spectroscopy (FTIR) spectral analysis.

MATERIALS AND METHODS

1. Materials

Balls of leaf sheaths of *P. oceanica* were collected from the Cap Zebib beach (North coast of Tunisia). The fibers were manually separated, washed with generous amounts of distilled water to remove the surface-adhered particles and then dried in an oven at 60 °C for 48 h to a constant weight. The dried fibers were chopped, sieved and the particles with an average of 0.5 mm were used for biosorption experiments.

2. Reagents and Equipment

A stock solution of copper was prepared by dissolving appropriate amount of anhydrous $Cu(NO_3)_2$ in 1 L of deionized water, and the concentrations of Cu(II) used in this study (10-400 mg L^{-1}) were obtained by dilution of the stock solution. The pH of the solutions was adjusted to the desired value by adding 0.1 M HNO_3 or 0.1 M NaOH solutions before mixing the dried biomass with the solution. The surface charge of the biomass was measured with a Zeta potential analyzer (Malvern Zetasizer nano ZS).The metal concentrations were analyzed by an atomic absorption spectrophotometer (SHIMADZU AA-680, Japan). Transform infrared (FT-IR) spectra of dried unloaded biomass and Cu(II)-loaded biomass prepared as KBr discs were recorded at 400-4,000 cm^{-1} wavenumber range with an FT-IR spectrometer (FTS-135).

3. Batch Biosorption Experiments

The biosorption equilibrium experiments of Cu(II) were performed by using a batch process to determine the amount of metal ion adsorbed by biomass samples under the effect of contact time, biosorbent dosage, pH and temperature of adsorption medium. Necessary amount of the dried biomass was equilibrated in a series of aqueous solutions (25 ml) placed in conical flasks containing different amounts of metal at a constant pH, which was adjusted with 0.1 M HNO_3 or 0.1 M NaOH solution at the beginning of each experiment. The flasks were shaken for the desired contact time in an electrically thermostatic reciprocating shaker (Selecta multimatic-55, Spain) at 100 rpm. The experiments were repeated at 293, 303, 313, and 323 K. The time required for reaching the equilibrium condition estimated by drawing samples at regular intervals of time till equilibrium was reached. The contents of the flask were filtered through filter paper, and the filtrate was analyzed for metal concentration by using flame AAS. The percent biosorption of metal ion was calculated as follows (Eq. (1)):

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

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

To ensure the accuracy, reliability and reproducibility of the collected data, the measurements were carried out in duplicate and the average values are presented. Throughout the study, the contact time was varied from 5 to 120 min, the pH from 2 to 8, the initial metal concentration from 10 to 400 mg/L, and the biosorbent dosage from 1 to 20 g/L.

4. Desorption Procedure

A sample volume of 25 mL, containing 10 mg/L of Cu(II), was transferred into a beaker; 10 mL of buffer solution was added. After a fast shaking, 4 g/L of *P. oceanica* was added and the mixture was shaken again for 60 min at 100 rpm. The system was filtered with blue band filter paper. Then the filter and constituents were washed with distilled water. To elute the sorbed analytes by *P. oceanica* 10 mL of 1 M HCl and 10 mL of 1 M HNO_3 were used separately. Analyte contents of the final solution were determined by AAS. The same procedure was applied to the blank solution. To use the biomass for the next experiment, the biomass was washed with excess of 1M acid solution and distilled water, sequentially.

RESULTS AND DISCUSSION

1. Effect of pH Solution

The pH of the aqueous solution is an important controlling parameter in the heavy metals adsorption processes, because it affects the solubility of metal ions and the concentration of the counter ions on the functional groups of the biomass cell walls [10].

Fig. 1 indicates that the maximum biosorption capacity of biomass was observed at pH 6. Under highly acidic conditions, copper(II) removal was inhibited. The biosorption yield of Cu(II) increased from 67% to 95% when the solution pH was increased from 2 to 6. It is well known that there is a close relationship between the zeta potential and the biosorption capacity of biomaterials [11]. Therefore, the zeta potentials of the biomass under different pH conditions were determined and the results are shown in Fig. 2.

When the pH of the solution was increased the number of positively charged available sites decreased. The surface of the biomass became negatively charged, and this increased the sorption of the positively charged copper(II) ions through electrostatic forces of attraction. It should be pointed out that when pH was higher than 4, carboxylic groups (-COOH) in *P. oceanica* were deprotonated and negatively charged. Consequently, the biosorption of copper(II)

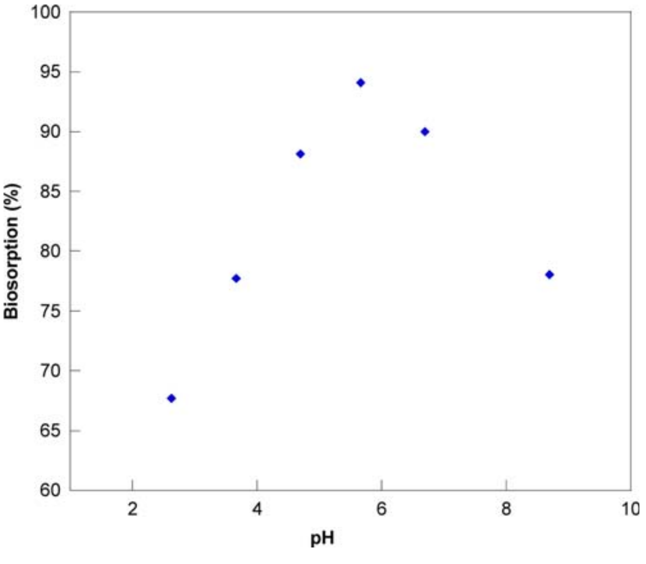

Fig. 1. Effect of pH on biosorption of Cu(II) onto onto *P. oceanica* (metal concentration: 10 mg/L; temperature: 20 °C).

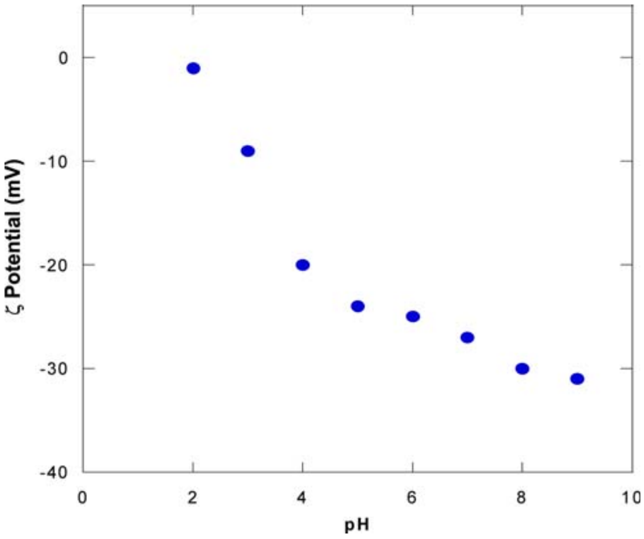

Fig. 2. Zeta potential of *P. oceanica* at various pH values.

was enhanced at higher pH values. The lower biosorption capacity of the biomass observed at acidic pH is due to the competition between the excess hydronium (H_3O^+) ions and the positively charged metal ions for the biosorption sites. Above pH 6, insoluble copper(II) hydroxide starts precipitating from the solution, so that biosorption yield was decreased [12]. As a result, the optimum pH for copper(II) biosorption was found as 6 and the other biosorption experiments were performed at this pH value.

2. Effect of Biomass Dosage

The biomass concentration is another important variable during metal uptake. Data obtained from the experiments with varying biosorbent concentrations are presented in Fig. 3.

The biosorption yield steeply increased with the biomass concentration up to 4 g/L. The observed enhancement in copper(II) biosorption yield with increasing biomass concentration was attributed to the availability of more sorption sites [13]. A further increase in biomass concentration over 4 g L^{-1} did not lead to a significant improvement in biosorption yield due to the saturation of the biosorbent surface with Cu(II) ions. Therefore, the optimal biomass concentration was selected as 4 g L^{-1} for the further experiments.

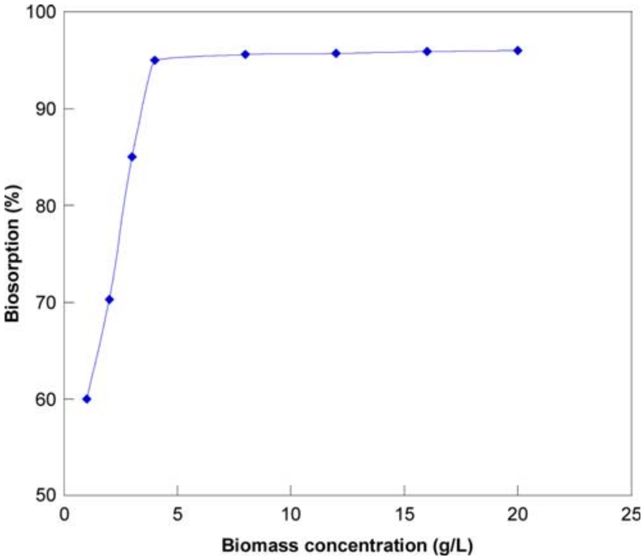

Fig. 3. Effect of biomass concentration on the biosorption of Cu(II) by *P. oceanica* biomass (metal concentration 10 mg/L; pH 6; temperature 20 °C).

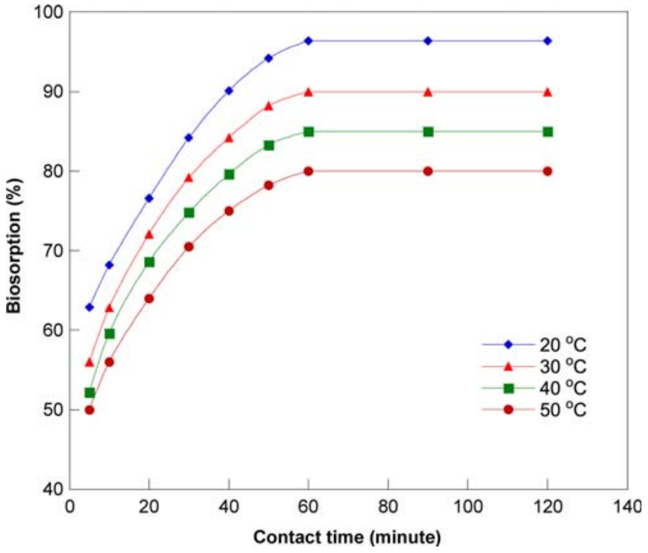

Fig. 4. Effect of contact time and temperature (metal concentration 10 mg/L; biomass dosage 4 g/L; pH 6).

3. Effects of Contact Time and Temperature

The rate of adsorption is a very important factor in the reactor design and the optimization process in industry. The effect of contact time on the biosorption of Cu(II) from aqueous solution is shown in Fig. 4.

According to this figure, the biosorption efficiency of Cu(II) ions increases with increase in contact time. The biosorption of Cu(II) ions is rapid in the first 30 min, as a result of free binding sites on the biomass. The biosorption approaches equilibrium within 60 min for copper(II) ions as the binding sites on the biomass are being used up. Biosorption of copper ions seems to follow two-phase sorption mechanism. The initial fast phase occurs due to a larger surface area of the biosorbent being available for the adsorption of the metal ions. The subsequent slow phase occurs due to quick exhaustion of the adsorption sites [14]. The optimum contact time is therefore selected as 60 min for further experiments. On the other hand, the biosorption percentage decreased from 96% to 80% as temperature was increased from 20 to 50 °C for the equilibrium time, 60 min. This result indicated the exothermic nature of Cu(II) biosorption onto *P. oceanica* biomass. The decreasing in biosorption efficiency may be attributed to either the damage of active binding sites in the biomass or the weakness of biosorptive forces between the active sites of the sorbents and the sorbate species [15,16]. The optimum temperature was selected as 20 °C for further biosorption experiments.

4. Biosorption Isotherms

Biosorption isotherms describe the relationship between the mass of the adsorbed component per biosorbent mass and the concentration of this component in the solution. Determination of equilibrium parameters provides important information that allows for future design of adsorption. Equilibrium isotherm for the biosorption of Cu(II) ions onto *P. oceanica* is presented in Fig. 5.

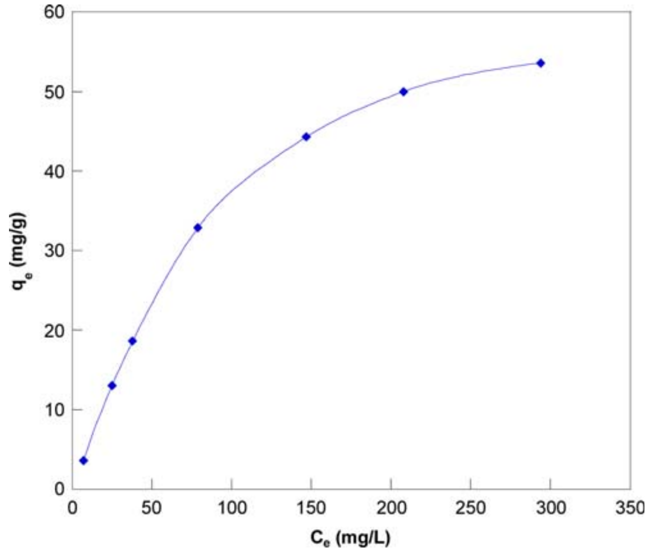

Fig. 5. Equilibrium isotherm for the biosorption of Cu(II) ions onto *P. oceanica* (biomass dosage: 4 g/L; contact time: 60 min; pH: 6; temperature: 20 °C).

From this figure, the biosorption capacity rises sharply with the increase of equilibrium concentration, and then it grows slightly, and finally approaches a maximum.

We used the Langmuir and Freundlich adsorption isotherm models to evaluate the equilibrium data. Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of uniform adsorption sites without migration of adsorbed molecules on the surface [17]. This model can be written in linear form:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}} \tag{2}$$

where q_e is the equilibrium metal ion concentration on the biosorbent (mg/g), C_e is the equilibrium metal ion concentration in the solution (mg/L), q_{max} is the monolayer biosorption capacity of the biosorbent (mg/g), and b is the Langmuir biosorption constant (L/mg) relating the free energy of adsorption. The values of q_{max} and Langmuir constant b were calculated from the slope and intercept of the linear plot of C_e/q_e vs C_e (Fig. 6).

As seen from the figure, the value of correlation coefficient (R^2= 0.998) shows that the biosorption of copper ions onto. *P. oceanica* biomass fitted well the Langmuir model, which indicates the formation of monolayer coverage of heavy metal ions on the outer surface of biosorbent. The maximum biosorption capacity (q_m) and Langmuir constant (b) were found to be 76.92 mg/g and 8.88×10^{-3}, respectively.

The Freundlich isotherm model describes the adsorption on heterogeneous surface and is not restricted to the formation of monolayer. The linear form of the Freundlich adsorption isotherm can be defined by the following equation [18]:

$$\log q_e = \log k_f + \frac{1}{n}\log C_e \tag{3}$$

where k_f a constant is related to the biosorption capacity and 1/n is an empirical parameter related to the biosorption intensity of the adsorbent. The Freundlich isotherm constants k_f and 1/n were calculated from the slopes and intercepts of the linear plot of $\log q_e$ versus $\log C_e$.

The values of k_f and 1/n were 1.12 and 0.73, respectively. The 1/n values were between 0 and 1, indicating that the biosorption of Cu(II) onto *P. oceanica* biomass was favorable at studied conditions. However, compared to the R^2 values, 0.977 with that obtained from the Langmuir model, it can be remarkably noted that the Langmuir isotherm model is better fitted the equilibrium data.

The Dubinin-Radushkevich isotherm is more general than the Langmuir isotherm since it does not assume a homogeneous surface or constant biosorption potential. It was applied to distinguish between the physical and chemical biosorption of Cu(II) [19].

The linear presentation of the D-R isotherm equation [20] is expressed by (Eq. (4)):

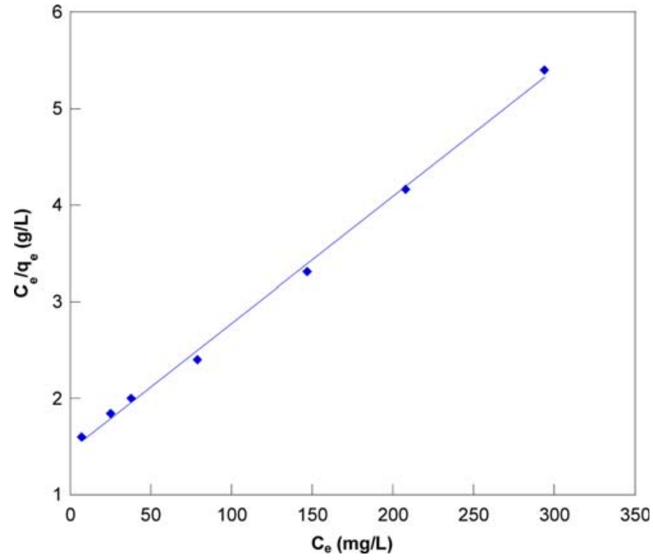

Fig. 6. Langmuir isotherm plots for biosorption of Cu(II) onto *P. oceanica* (biomass dosage: 4 g/L; contact time: 60 min; pH: 6; temperature: 20 °C).

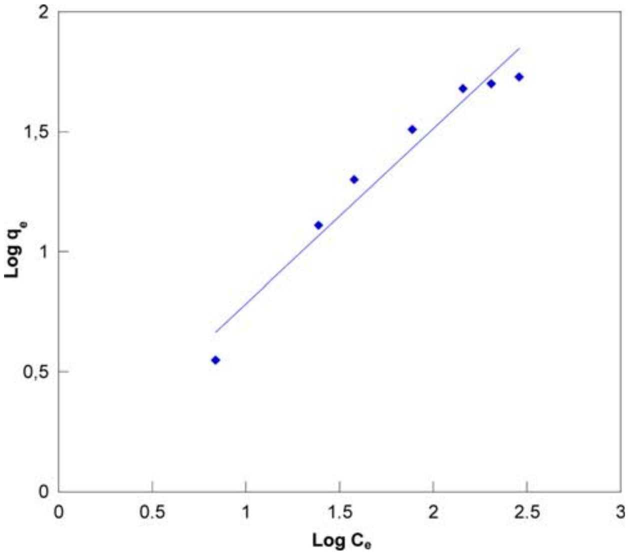

Fig. 7. Freundlich isotherm plots for biosorption of Cu(II) *P. oceanica* (biomass dosage: 4 g/L; contact time: 60 min; pH: 6; temperature: 20 °C).

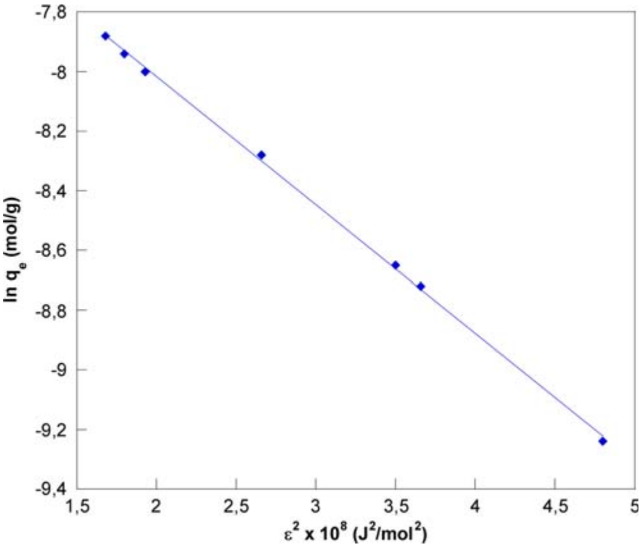

Fig. 8. D-R isotherm plots for adsorption of Cu(II) onto *P. oceanica* (biomass dosage 10 g/L; contact time 60 min; pH 6; temperature 20 °C).

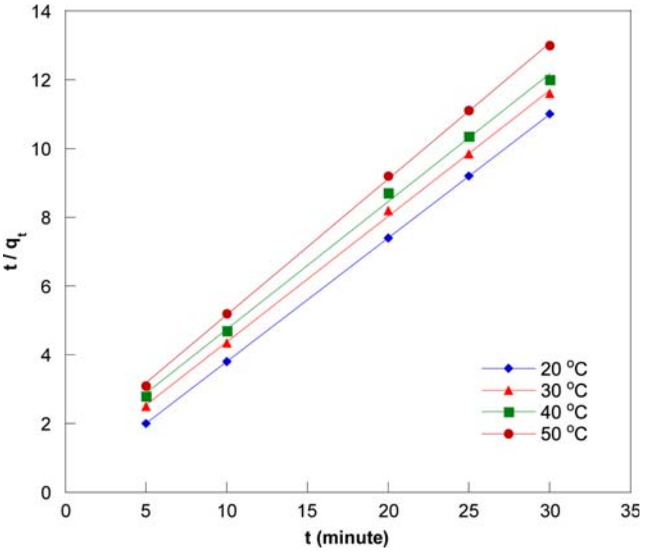

Fig. 9. Pseudo-second-order kinetic plots at different temperatures (pH: 6; biosorbent dosage: 4 g/L; contact time: 60 min; temperature:20 °C).

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \tag{4}$$

where q_e is the amount of metal ions adsorbed on per unit weight of adsorbent (mol/L), q_m is the maximum adsorption capacity (mol/g), β is the activity coefficient related to adsorption mean free energy (mol^2/J^2) and ε is the Polanyi potential [$\varepsilon = RT \ln(1+1/C_e)$].

The D-R isotherm model well fitted the equilibrium data since the R^2 value was found to be 0.999 (Fig. 6). From the intercept of the plots, the q_m value was found to be 7.8×10^{-4} mol/g. The adsorption mean free energy (E, kJ/mol) is as follows:

$$E = \frac{1}{\sqrt{-2\beta}} \tag{5}$$

The E (kJ/mol) value gives information about adsorption mechanism, physical or chemical. If it is between 8 and 16 kJ/mol, the adsorption process takes place chemically, and while E<8 kJ/mol, the adsorption process proceeds physically [20]. The mean adsorption energy was calculated as 10.78 kJ/mol for the adsorption of Cu(II)) ions. These results indicated that the adsorption processes of Cu(II) ions onto *P. oceanica* biomass may be carried out via chemisorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate [21].

5. Adsorption Kinetics Study

The prediction of biosorption rate gives important information for designing batch biosorption systems. Information on the kinetics of pollutant uptake is required for selecting optimum operating conditions for a full-scale batch process.

To investigate the mechanism of adsorption at different initial concentrations and different temperatures, characteristic constants of adsorption rate were determined by using a pseudo first-order equation of Lagergren based on solid capacity, and pseudo second-order equation based on solid phase adsorption.

The linearized form of the pseudo-first-order rate equation by Lagergren [22] is given as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{6}$$

where q_t and q_e (mg/g) are the amounts of the metal ions biosorbed at equilibrium (mg/g) and t (min), respectively, and k_1 is the rate constant of the equation (min^{-1}). The values of the rate constant, k_1, equilibrium adsorption capacity, q_e, and the correlation coefficient, R^2, were calculated from the plots of $\log(q_e - q_t)$ versus t (figure is not shown) (Table 1).

Kinetic data were further treated with pseudo-second-order kinetic model which is given in the following form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{t}{q_2} \tag{7}$$

where k_2 ($gmg^{-1}\ min^{-1}$) is the rate constant of adsorption, q_2 is maxi-

Table 1. Pseudo-first-order and pseudo-second-order parameters for the biosorption of Cu(II) onto *P. oceanica* biomass at different temperatures

Temperature (°C)	$q_{e,exp}$ ($mg\cdot g^{-1}$)	Pseudo-first-order			Pseudo-second-order		
		k_1 (min^{-1})	$q_{e,cal}$ ($mg\cdot g^{-1}$)	r^2	k_2 ($g\cdot mg^{-1}\cdot min^{-1}$)	$q_{e,cal}$ ($mg\cdot g^{-1}$)	r^2
20	2.41	$41.5.10^{-2}$	1.36	0.964	0.26	2.78	0.999
30	2.25	$18.3.10^{-2}$	1.25	0.978	0.18	2.72	0.998
40	2.12	$15.6.10^{-2}$	1.14	0.956	0.14	2.68	0.998
50	2	$11.1.10^{-2}$	1,02	0.963	0.12	2.53	0.998

mum adsorption capacity (mg g^{-1}) [23]. The values of k_1, q_e and k_2, q_2 were obtained from the slopes and intercepts of plots of $\log(q_e - q_t)$ versus t and t/q_t versus t at different temperatures.

The linear plots of t/q_t versus t for the pseudo-second-order model for the biosorption of Cu(II) ions onto *P. oceanica* biomass at 20-50 °C are shown in Fig. 9.

The pseudo-first-order and pseudo-second-order parameters for the biosorption of Cu(II) onto *P. oceanica* biomass at different temperatures are given in Table 1.

Clearly, the correlation coefficients (R^2>0.99) for the pseudo-second-order kinetic model are higher in comparison with the pseudo-first-order kinetic model, and the calculated values of $q_{e,calc}$ from the pseudo-second-order kinetic model are very close to the experimental values ($q_{e,exp}$), for all studied heavy metals. These indicate clearly that the pseudo-second-order kinetic model was better in describing the biosorption kinetics of Cu(II) onto *P. oceanica* biomass.

6. Thermodynamic Parameters

To describe the thermodynamic behavior of the biosorption of Cu(II) onto *P. oceanica* biomass, thermodynamic parameters including the change in free energy (ΔG^0), the enthalpy (ΔH^0) and the entropy (ΔS^0) were calculated from the following equations [24,25]:

$$\ln K_D = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad \text{(van't Hoff equation)} \tag{8}$$

$$\Delta G^o = -RT \ln K_D \tag{9}$$

where $K_D = (q_e/C_e)$ is the adsorption equilibrium constant, T is absolute temperature (K), R is gas constant [26,27]. When $\ln K_D$ versus 1/T is plotted (Fig. 10), ΔH^0 and ΔS^0 values can be computed from slope and intercept of the van't Hoff equation. The calculated parameters are given in Table 2.

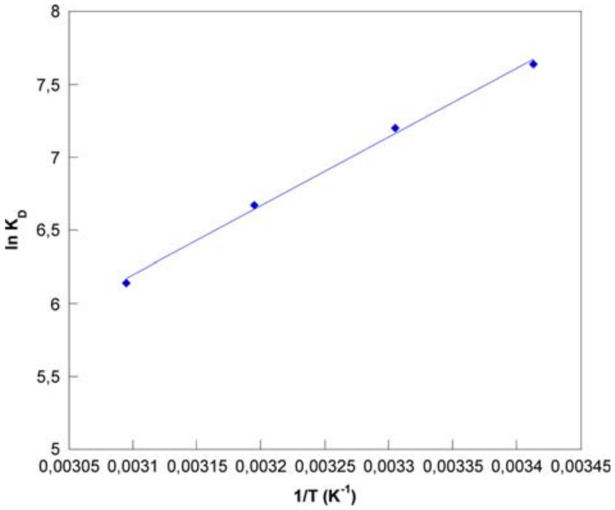

Fig. 10. Determination of thermodynamic parameters for biosorption of Cu(II) onto *P. oceanica* biomass.

Table 2. Thermodynamic parameters for Cu(II) biosorption onto *P. oceanica* biomass

T (k)	ΔG^0 (kJmol^{-1})	ΔH^0 (kJmol^{-1})	ΔS^0 (Jmol^{-1}k^{-1})
<u>**Cu(II)**</u>			
293	−18.71	−39.27	−70.17
303	−18		
313	−17.3		
323	−16.6		

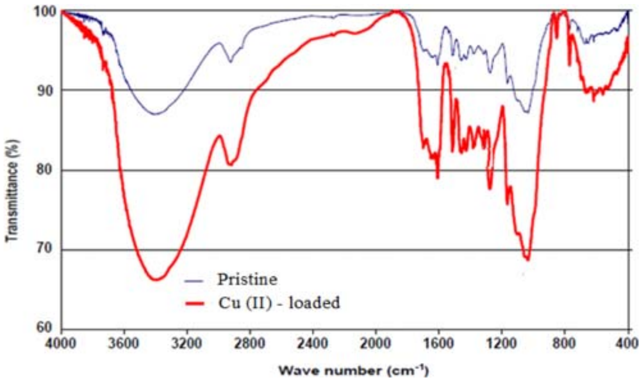

Fig. 11. FTIR spectrum of pristine and Cu(II)-loaded biomass *P. oceanica.*

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

The negative ΔH^0 is an indicator of the exothermic nature of the biosorption, and also its magnitude gives information on the type of biosorption, which can be either physical or chemical. Therefore, the ΔH^0 values showed that the biosorption processes of Cu(II) ions onto *P. oceanica* biomass occurred via chemisorption [28]. The negative ΔS^0 value (−70.17 J/mol K) suggests a decrease in the randomness at the solid/solution interface during the biosorption process [29].

7. FTIR Analysis

Fig. 11 shows the FTIR spectra of pristine and copper-loaded biomass samples. The peak at 3,422 cm^{-1} was due to bounded hydroxyl (-OH) or amine (-NH) groups. The peaks at 2,928 and 2,866 cm^{-1} were assigned to the -CH stretching groups. The bands observed at 1,720 and 1,672 cm^{-1} were attributed to C=O stretching group. The peak located at 1,613 cm^{-1} could be imputed to N-H bending. The bands at 1,318, 1,168 and 1,038 cm^{-1} were assigned to C-N stretching. The bands 1,467, 854 and 772 cm^{-1} were attributed to the C-H bending.

The asymmetrical stretching vibration at 3,422 cm^{-1} was shifted to 3,410 cm^{-1} after the biosorption of Cu(II). The changes in -OH adsorption peak indicated that the hydroxyl group had been changed from multimer to monopolymer or even dissociative state [30], which showed that the degree of the hydroxyl polymerization in biomass was decreased by binding of Cu(II). It offered more opportunity for Cu(II) to be bound to the hydroxyl or amine groups.

The peaks attributed to C=O stretching group at 1,720 and 1,672 cm^{-1} were observed at 1,703 and 1,657 cm^{-1} after Cu(II) sorption. The spectral analysis before and after metal binding indicated that the -CH was also involved in metal biosorption. There were clear band shifts and intensity decrease of the -CH band at 2,928-2,942 cm^{-1}. These results indicated that the O-H, -NH, C=O, C-H and N-H groups are responsible for the binding of the metal ions.

8. Comparison of Cu(II) Removal with Different Biosorbents Reported in the Literature

The sorption capacity of *P. oceanica* biomass for Cu(II) was com-

Table 3. Comparison of biosorption capacity of *P. oceanica* biomass for Cu(II) with that of other biosorbents

Biosorbent	pH	Temperature (°C)	q_m (mg/g)	References
Wheat shell	6	20	7.39	[12]
Suggar beet pulp	4	25	28.5	[29]
Tea waste	5-6	22	48	[31]
Peanut hull	5.5	30	21.25	[32]
Biocarrier beads	-	20	0.559	[33]
P. oceanica	6	20	76.92	Present study

pared with other adsorbents reported in the literature and the biosorption capacities are presented in Table 3.

Values are reported in the form of monolayer adsorption capacity. Biosorption capacity varies and depends on the characteristics of the individual adsorbent, the extent of surface/surface modification and the initial concentration of the adsorbate. As can be seen from Table 3, the biosorption capacity of *P. oceanica* for Cu(II) was found to be comparable and moderately higher than that of other sorbent materials reported in literature [12,29,31-33].

Therefore, the *P. oceanica* biomass has a great potential for the removal of Cu(II) ions from aqueous solution.

9. Desorption Efficiency

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 [34].

Desorption of Cu(II) from the *P. oceanica* biomass was studied separately using 1 M HCl (10 mL) and 1 M HNO_3 (10 mL). The highest desorption efficiency was achieved as about 95% and 78% using 1 M HCl and 1 M HNO_3, respectively.

As also seen in Fig. 12, the high stability of *P. oceanica* biomass permitted ten-times of biosorption-desorption process along with the studies with a decrease about 20% in biosorption efficiency of Cu(II). These results indicate that the *P. oceanica* biomass offers potential to be used repeatedly for removal of Cu(II) from aqueous solutions.

CONCLUSIONS

This work demonstrates the feasibility of using *P. oceanica* biomass for the biosorption of Cu(II) ions. The batch study parameters such as pH of solution, biosorbent dosage, contact time, and temperature are found to be effective in the biosorption process. The desired pH value for biosorption was found to be 6. The maximum uptake of Cu(II) by *P. oceanica* biomass was estimated to be 76.92 mg/g. Langmuir isotherm model shows better fit to the sorption data of Cu(II) than the Freundlich isotherm model. The mean free energy value (10.78 kJ/mol) obtained from the D-R model indicated that the biosorption of Cu(II) ions onto *P. oceanica* was via chemical ion-exchange. The biosorption rate of Cu(II) ions is very fast and the equilibrium is achieved after 60 min. The kinetics of the process is well described using the pseudo-second order model. The calculated thermodynamic parameters show the feasibility, exothermic and spontaneous nature of the biosorption of Cu(II) ions onto *P. oceanica*. The results of FTIR revealed that carboxyl, amine, and hydroxyl groups on the biomass surface were involved in the biosorption of Cu(II) ions. This study has illustrated an alternative solution for the management of unwanted biological materials where *P. oceanica*, fast-growing marine fibers, could be, to some extent, utilized as a biosorbent for the removal of heavy metals from low-strength wastewater.

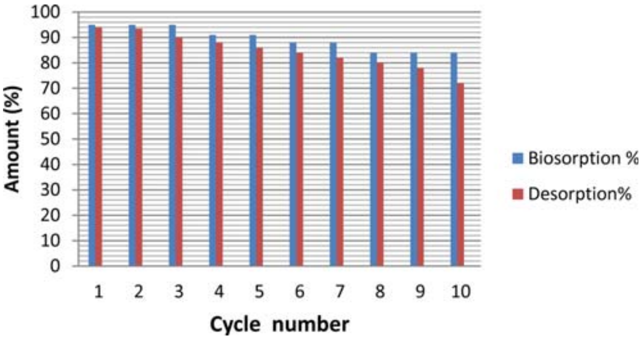

Fig. 12. Biosorption–desorption efficiency with cycle number (biomass concentration: 4 g/L; contact time: 60 min; temperature: 20 °C).

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