Biosorptive removal of mercury(II) from aqueous solution using lichen (*Xanthoparmelia conspersa*) biomass: Kinetic and equilibrium studies

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ARTICLE INFO

ABSTRACT

The potential use of the lichen biomass (*Xanthoparmelia conspersa*) to remove mercury(II) ions from aqueous solution by biosorption was evaluated using the batch method. Effects of pH, contact time, biomass concentration and temperature on the removal of Hg(II) ions were studied. The Langmuir isotherm models defined the equilibrium data precisely compared to Freundlich model and the maximum biosorption capacity obtained was $82.8 \, mg \, g^{-1}$. From the D–R isotherm model, the mean free energy was calculated as $9.5 \, kJ \, mol^{-1}$. It shows that the biosorption of Hg(II) ions onto *X. conspersa* biomass was taken place by chemical ion-exchange. Experimental data were also performed to the pseudo-first-order and pseudo-second-order kinetic models. The results indicated that the biosorption of Hg(II) on the lichen biomass followed well the second-order kinetics. Thermodynamic parameters, ΔG^o, ΔH^o and ΔS^o indicated the Hg(II) sorption to be exothermic and spontaneous with decreased randomness at the solid–solution interface. Furthermore, the lichen biomass could be regenerated using 1 M HCl, with up to 85% recovery, which allowed the reuse of the biomass in ten biosorption–desorption cycles without any considerable loss of biosorptive removal capacity.

1. Introduction

In recent years, the presence of heavy metals in industrial wastewater and effluents is an important environmental problem due to their more stringent discharge norms, increased usage and their high toxicity cumulative adverse characteristics [1]. This problem has received considerable amount of attention in recent years. One primary concern is that marine animals which can readily adsorb those heavy metals in wastewater and directly enter the human food chains present a high health risk to consumers.

Mercury is a pervasive contaminant that is highly toxic and is readily accumulated by organisms [2,3]. The major effects of mercury poisoning are neurological and renal disturbances as well as impairment of pulmonary function [4]. Natural inputs of mercury to the environment are related to weathering of mercuriferous areas, the degassing from surface water and from the earth's crust through volcanic eruptions, naturally caused forest fires, and biogenic emissions [5]. In addition, this metal is also released to the environment from anthropogenic activities that include agriculture, battery production, fossil fuel burning, mining and metallurgical processes, paint and chloralkali industries, and wood pulping [6]. The maximum permissible limit of Hg^{2+} ions in drinking water is 0.001 mg/L [7].

In view of the toxicity and in order to meet regulatory safe discharge standards, it is essential to remove heavy metals from wastewaters/effluents before it is released into the environment [8,9]. A number of technologies have been developed over the years to remove toxic metal ions from water. Conventional methods for the removal of heavy metals include ion-exchange, chemical precipitation, reverse osmosis, evaporation, membrane filtration, adsorption biological treatment [10]. These techniques are often ineffective or expensive, especially when concentrations are in the order of 1–100 mg/L. New technologies are required that can reduce heavy metal concentrations to environmentally acceptable levels at reasonable cost. Biosorption has the potential to greatly contribute to the achievement of this goal. This method plays an important role in the elimination of metal ions from aqueous solutions [11,12]. The main advantages of this technique are the reusability of biomaterial, low operating cost, improved selectivity for specific metals of interest, removal of heavy metals from effluent irrespective of toxicity, short operation time, and no production of secondary compounds which might be toxic [13]. Various biomasses have been used for the removal of Hg(II) ions from aqueous solution [13,14].

Lichens are composite plants composed of fungi and algae [15] and they are considered as indicator of environmental quality due to their accumulating and retaining ability of a variety of con-

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taminants, particularly heavy metals and radionuclides [16–18]. The lichen (*Xanthoparmelia conspersa*) biomass has a bright green colour. It contains fungal and algal cells (the two components that make up a lichen). As far as the authors are aware, there is no investigation reported in the literature on the biosorption of Hg(II) by *X. conspersa*. In addition, this new material was chosen as biosorbent in this study due to its natural, easily available and thus low-cost biomass for dissolved metal ions.

The objective of the present work is to investigate the potential use of the *X. conspersa* biomass to remove Hg(II) ions from aqueous solution by biosorption using the batch method. Optimum biosorption conditions were determined as a function of pH, biomass dosage, contact time, and temperature. The Langmuir, Freundlich and Dubinin–Radushkevich (D–R) models were used to describe equilibrium isotherms. The biosorption mechanisms of Hg(II) ions onto *X. conspersa* biomass were also evaluated in terms of thermodynamics and kinetics.

2. Experimental procedures

2.1. Biomass preparation

The lichen biomass (*X. conspersa*) sample was collected from the Black Sea coast of Turkey. Samples were washed with deionised water and inactivated by heating in an oven at 80 °C for 48 h. The inactivated dried lichen biomass was ground and sieved through different sizes and 180–300 μm fraction was used in all experiments.

2.2. Reagents and equipments

Analytical reagent grade chemicals were used in this study. Double deionised water (Milli-Q Millipore 18.2 MΩ cm⁻¹ conductivity) was used for all dilutions. A pH meter, Sartorius pp-15 Model glass-electrode was employed for the measurement of pH values in the aqueous phase. Phosphate buffer solution ($H_2PO_4^-$/H_3PO_4) was prepared by mixing appropriate volumes of $1\,mol\,L^{-1}$ sodium dihydrogen phosphate and phosphoric acid solutions for pH 2. Acetate buffer solutions (CH_3COO^-/CH_3COOH) were prepared by mixing appropriate volumes of $1\,mol\,L^{-1}$ acetic acid and $1\,mol\,L^{-1}$ sodium acetate solutions for pH 4. Phosphate buffer solutions ($H_2PO_4^-$/HPO_4^{2-}) were prepared by mixing appropriate volumes of $1\,mol\,L^{-1}$ sodium dihydrogen phosphate and $1\,mol\,L^{-1}$ sodium hydrogen phosphate for pH 5 and 6. Ammonium buffer solutions were prepared by mixing appropriate amounts of $1\,mol\,L^{-1}$ ammonia and $1\,mol\,L^{-1}$ ammonium chloride solutions for pH 8–10.

Perkin Elmer Analyst 700 model AAS equipped with MHS 15 CVAAS system was used for mercury determination. A hallow cathode lamp operating at 6 mA was used and a spectral bandwidth of 0.7 nm was selected to isolate the 253.7 nm mercury line. NaBH₄ (1.5%) (w/v) in NaOH (0.5%) (w/v) was used as reducing agent. The analytical measurement was based on peak height. Reading time and argon flow rate were selected as 10 s and 50 mL min⁻¹, respectively. Fourier Transform Infrared (FT-IR) spectra of dried unloaded biomass and Hg(II)-loaded biomass were recorded using a FT-IR spectrometer (JASCO-430, Japan).

2.3. Batch biosorption procedure

A 1000 mg/L stock solution of Hg(II) was prepared by HgCl₂ (Merck). Biosorption experiments were conducted using the solutions having 10 mg/L of Hg(II) with the optimum biomass concentration, 4 g/L.

The solutions (25 mL) including the biomass were shaken for the desired contact time in an electrically thermostatic reciprocating

shaker (Selecta multimatic-55, Spain) at 120 rpm. The batch studies were performed at different experimental conditions such as initial metal concentration (10–400 mg/L), contact time (5–120 min), pH (2–8), biomass concentration (0.4–16 g/L), and temperature (20–50 °C). The equilibrium time was estimated by drawing samples at regular intervals of time till equilibrium was reached. The contents of the flask were filtered through 0.25 μm filter (Double rings, China). The metal concentration of filtrate was analyzed using CVAAS. Each determination was replicated three times and the mean results are considered in the analysis. The percent biosorptive removal of the metal ion was calculated as follows:

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

where C_i and C_f are the initial and final metal ion concentrations, respectively.

2.4. Desorption procedure

The desorption studies of Hg(II) from the biosorbent was carried out by using 1 M HNO₃ (10 mL) and 1 M HCl (10 mL). After the determination of metal content of the final solutions, the biosorbent was washed with excess of the acid solution and distilled water in order to reuse for next experiment. Consecutive sorption–desorption cycles were repeated ten times to establish the reusability of the biosorbent for Hg(II) removal from aqueous solution.

2.5. Statistical analysis

Batch experiments were conducted in replicates ($N = 3$) and data represent the mean value. The metal sorption and final solution concentration data were fitted to Langmuir and Freundlich isotherm models using non-linear regression analysis and D–R isotherm model using linear regression analysis (SigmaPlot Version 7.0). The best-fit values for each variable in the models were determined along with, determination of coefficient, standard errors (SE) and coefficients of variation (CV% = SE × 100/parameter value) are tabulated in the following section. For the determination of intergroup mean value differences, each parameter was subjected to the Student's *t*-test for significance level ($p < 0.05$).

3. Results and discussion

3.1. FT-IR analysis

The functional groups responsible for the biosorption of heavy metal ion on the cell surfaces of biosorbent are confirmed by FT-IR spectra. The FT-IR spectra of unloaded and Hg(II)-loaded lichen biomass were obtained (Fig. 1). The FT-IR spectra of the lichen biomass indicate the presence of amino, carboxylic, hydroxyl and carbonyl groups. The broad bands at 3486, 3424, 3346, and 3258 cm⁻¹ are dominated by —OH and —NH stretching. The peaks at 1621 and 1455 cm⁻¹ are caused by the stretching band of carboxyl (—C=O) groups. The bands observed at 1039 and 1145 cm⁻¹ were assigned to P=O stretching P—OH stretching vibrations. The peaks at 2928, 1430, and 1376 cm⁻¹ representing C—H stretching vibrations, N—H bending, —CH₃ wagging vibrations, respectively, are due to the several functional groups present on the cell surfaces of lichen biomass. The peaks at 781, 662, and 518 cm⁻¹ are caused by C—N—C scissoring, which are found in polypeptide structure.

From Fig. 1, it can also be observed that the small shifts were occurred in the absorbance of some peaks obtained for the Hg(II)-loaded lichen biomass compared with that of the unloaded lichen biomass. The bands observed at 3424, 3346, and 3258 cm⁻¹ were shifted to 3428, 3336, and 3258 cm⁻¹, respectively. The peak

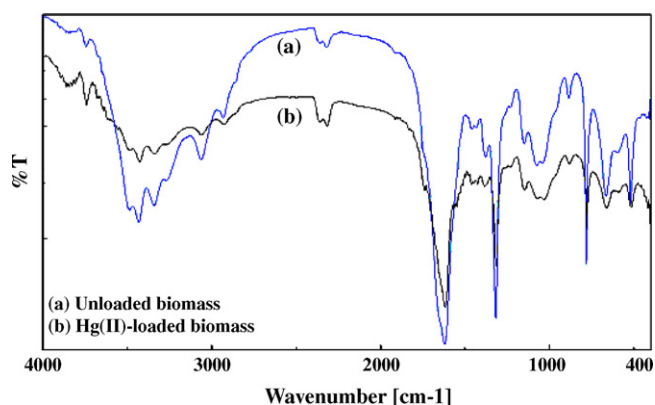**Fig. 1.** FT-IR spectrum of unloaded and Hg(II)-loaded biomass.

stretching band of carboxyl (—C═O) groups was shifted from 1621 to 1617 cm^{-1}. The stretching bands observed at 1039 and 1145 cm^{-1} were shifted to 1032 and 1148 cm^{-1}, respectively. The analysis of the FT-IR spectral results showed that the these functional groups above mentioned are responsible for the binding of the metals to cell surfaces of the lichen biomass. The parallel results were reported for the biosorption of Hg(II) by algae and fungi biomasses which have the same functional groups [19,20]. In addition, the similar FT-IR results were found for the heavy metal biosorption using different kinds of lichen biomasses [17,18].

3.2. Effect of pH

One of the more important factors affecting biosorption of metal ions is pH of solution. The acidity of the medium affects the competition ability of hydrogen ions with metal ions to active sites on the biosorbent surface [21].

The effect of pH on the biosorption of Hg(II) ions onto *X. conspersa* biomass was studied by changing pH values in the range of 2–8 and the results were presented in Fig. 2. At low pH values (2–4), the number of negatively charged surface sites decreased and the number of positively charged sites increased, which did not favor the sorption of positively charged metal ions (Hg^{2+} and Hg(OH)$^+$) due to electrostatic repulsion. Additionally, lower biosorption of Hg(II) at acidic pH is due to the presence of excess H$^+$ ions compet-
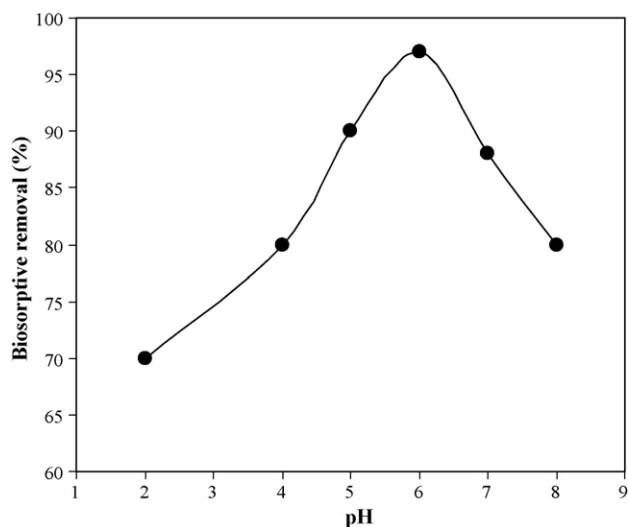

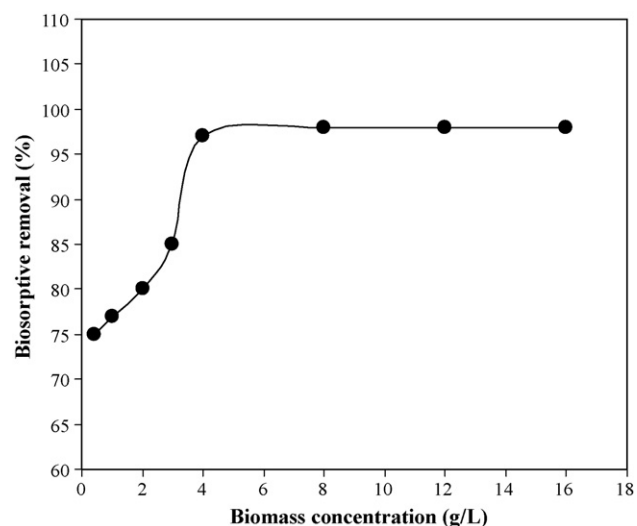**Fig. 3.** Effect of biomass concentration on the biosorption of Hg(II) onto *X. conspersa* biomass (pH: 6, volume of solution: 25 mL, initial concentration: 10 mg/L, contact time: 60 min, temperature: 20 °C and $N = 3$).

ing with metal ions for the sorption sites. The increased biosorption in the pH range 2–6 is also due to the less competition from protons to reaction sites, to an increase in concentration of Hg(OH)$^+$ species. At high pH values (6–8), the decrease in biosorption is due to the formation of soluble hydroxylated compound (Hg(OH)$_2$). The maximum Hg(II) removal was found to be 97% at pH 6 and therefore all the biosorption experiments were carried out at this pH value.

3.3. Effect of biomass concentration

The biosorption efficiency for Hg(II) ions as a function of biomass concentration was investigated (Fig. 3). The percentage of the biosorptive removal steeply increases with the biomass loading up to 4 g/L. This is due to the increase in active sites on the adsorbent and thus making easier penetration of the metal ions to the sorption sites. The maximum biosorptive removal was found to be 97% as biomass concentration was 4 g/L. The percent removal was almost same at higher dosages, 8, 12, and 16 g/L. This result can be explained as a consequence of a partial aggregation, which occurs at higher biomass dosage giving rise in a decrease of active sites on the biomass [22]. A further increase in biomass concentration over 4 g/L did not lead to a significant improvement in biosorptive removal due to the saturation of the biosorbent surface with Hg(II) ions. Therefore, the optimal biomass concentration was selected as 4 g/L for the further experiments.

3.4. Effects of contact time and temperature

Contact time is one of the important parameters for successful use of a biomass for practical application and rapid sorption is among desirable parameters. Fig. 4 shows the effect of contact time on the biosorptive removal of Hg(II) ions onto *X. conspersa*. It can be seen that the percent removal rapidly increases with rise in contact time up to 60 min at 20–50 °C. The rapid biosorption rate at the beginning of biosorption process may be explained by an increase in the number of active metal binding sites on the biosorbent surface, which would result in an increased concentration gradient between sorbate in the solution and on the biomass surface. After an increase in contact time, the occupation of the remaining vacant sites will be difficult due to the repulsive forces between the Hg(II) ions on the solid and the liquid phases.
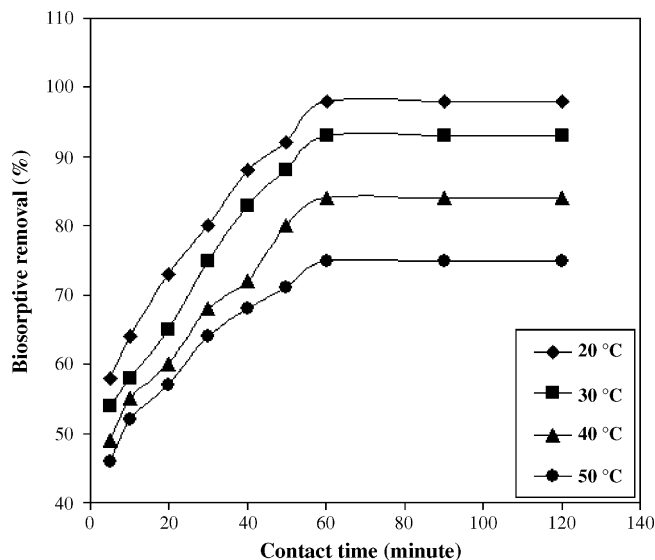

Fig. 2. Effect of pH on the biosorption of Hg(II) onto *X. conspersa* biomass (biomass concentration: 4 g/L, volume of solution: 25 mL, initial concentration: 10 mg/L, contact time: 60 min, temperature: 20 °C and $N = 3$).

Fig. 4. Effect of contact time and temperature on the biosorption of Hg(II) onto *X. conspersa* biomass (pH: 6, biomass concentration: 4 g/L, volume of solution: 25 mL, initial concentration: 10 mg/L and $N = 3$).

Temperature of the medium affects the removal efficiency of the pollutant from aqueous solution. Fig. 4 also shows the biosorption of Hg(II) ions as a function of the temperature. The percentage removal decreased from 98 to 75% as temperature was increased from 20 to 50 °C for the equilibrium time, 90 min. The observed trend with increasing temperature suggests that biosorptive removal process of mercury by the lichen biomass is kinetically controlled by an exothermic process. The optimum temperature was selected as 20 °C for further biosorption experiments.

3.5. Biosorption isotherm models

Biosorption isotherms are important for the description of how biosorbate will interact with a biosorbent and are critical in optimizing the use of biosorbent. In order to investigate the biosorption isotherms, three equilibrium models, which are namely the Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models were analyzed.

The Langmuir model suggests monolayer sorption on a homogeneous surface without interaction between sorbed molecules. This model can be written in non-linear form as follows [23].

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2}$$

where q_e is the equilibrium metal ion concentration on the sorbent (mg g^{-1}), C_e is the equilibrium metal ion concentration in the solution (mg/L), q_m is the monolayer sorption capacity of the sorbent (mg g^{-1}), and K_L is the Langmuir sorption constant (L mg^{-1}) relating the free energy of sorption.

Fig. 5 indicates the non-linear relationship between the amount (mg) of Hg(II) ions sorbed per unit mass (g) of *X. conspersa* biomass against the concentration of Hg(II) ions remaining in solution (mg/L).

The model parameter values and their statistical analysis data are given in Table 1. As seen from this table the coefficient of determination has high value ($R^2 = 0.996$). The SE values for both the K_L and q_m parameters are low and the coefficients of variation (CV) values are less than 10% for both parameters. Based on these results, it can be noted that the mercury biosorption onto *X. conspersa* biomass fitted well the Langmuir model. In other words, the sorption of Hg(II) ions onto *X. conspersa* was taken place at the functional groups/binding sites on the surface of the biomass which
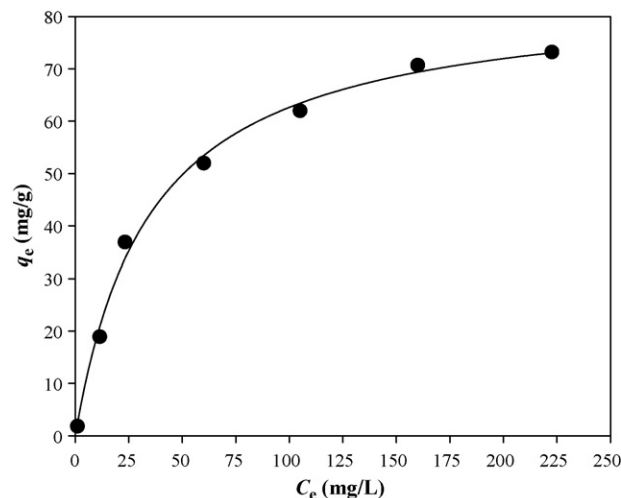

Fig. 5. Langmuir isotherm plots for the biosorption of Hg(II) onto *X. conspersa* biomass (pH: 6, biomass concentration: 4 g/L, volume of solution: 25 mL, initial concentration: 10–400 mg/L, contact time: 60 min, temperature: 20 °C and $N = 3$).

is regarded as monolayer biosorption. The maximum biosorption capacity (q_m) of *X. conspersa* biomass was found to be 82.8 mg g^{-1}.

The Freundlich isotherm model proposes a monolayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between sorbed molecules. The Freundlich model [34] is

$$q_e = K_f C_e^{1/n} \tag{3}$$

where K_f is a constant relating the sorption capacity and $1/n$ is an empirical parameter relating the sorption intensity, which varies with the heterogeneity of the material.

Fig. 6 shows the non-linear Freundlich isotherms obtained for the biosorption of Hg(II) ions onto *X. conspersa* biomass.

The model parameter values and their statistical analysis data are given in Table 1. As seen from this table the coefficient of determination has low value ($R^2 = 0.960$). The SE values for both the K_f and $1/n$ parameters are high and the CV values are more than 10% for both parameters. These results indicate that the Freundlich model was not able to adequately describe the relationship between the amount of Hg(II) adsorbed by the biomass and its equilibrium concentration in the solution.

The equilibrium data were also subjected to the D–R isotherm model to determine the nature of biosorption processes as physical or chemical. The results were shown in Fig. 7 and Table 1. The linear form of the D–R isotherm equation [35] is:

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

where q_e is the amount of metal ions adsorbed on per unit weight of biomass (mol g^{-1}), q_m is the maximum biosorption

Table 1
The Langmuir, Freundlich and D–R model parameters and their statistical analysis data.

| Parameter	Value	R^2	SE	CV (%)
Langmuir model parameters				
q_m (mg g^{-1})	82.5	0.996	0.861	1.043
K_L (L mg^{-1})	0.029		0.003	10.06
Freundlich model parameters				
K_f	9.486	0.960	2.463	25.96
$1/n$	0.392		0.0054	13.76
D–R model parameters				
$\ln q_m$	−6.293	0.991	0.118	1.879
β	-5.559×10^{-9}		-2.339×10^{-10}	4.208
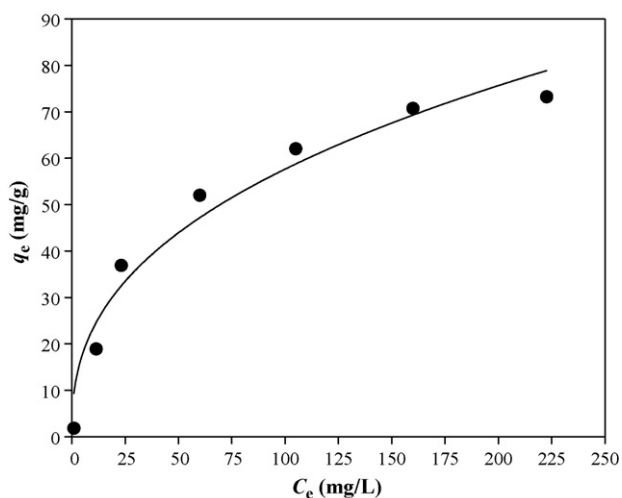
Fig. 6. Freundlich isotherm plots for the biosorption of Hg(II) onto *X. conspersa* biomass (pH: 6, biomass concentration: 4 g/L, volume of solution: 25 mL, initial concentration: 10–400 mg/L, contact time: 60 min, temperature: 20 °C and $N = 3$).

capacity $(mol\,g^{-1})$, β is the activity coefficient related to biosorption mean free energy $(mol^2\,J^{-2})$ and ε is the Polanyi potential $(\varepsilon = RT\ln(1 + 1/C_e))$. The D–R model parameter values and their statistical analysis data are given in Table 1. As seen from this table the coefficient of determination was found to be 0.991. The SE values for the parameters are low and the CV values are less than 10% for both parameters. From this table, q_m value was also found to be $1.849 \times 10^{-3}\,mol\,g^{-1}$.

The mean free energy $(E;\,kJ\,mol^{-1})$ is calculated by using β value [36]

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

The $E\,(kJ\,mol^{-1})$ value gives information about adsorption mechanism, physical or chemical. If it lies between 8 and 16 kJ mol^{-1}, the adsorption process takes place chemically, while, $E < 8\,kJ\,mol^{-1}$, the adsorption process proceeds physically [37,38]. The mean biosorption energy was calculated as 9.483 kJ mol^{-1} for the biosorption of Hg(II) ions. This result suggests that the biosorption processes
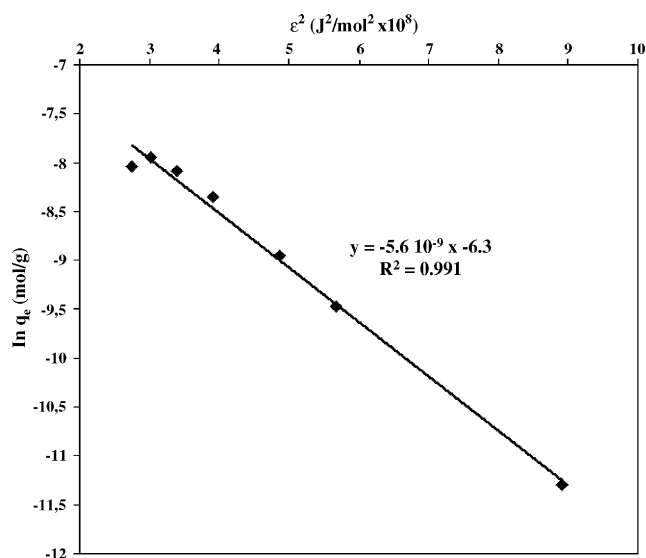
Fig. 7. D–R isotherm plots for the biosorption of Hg(II) onto *X. conspersa* biomass (pH: 6, biomass concentration: 4 g/L, contact time: 60 min, initial concentration:10–400 mg/L, contact time: 60 min, temperature: 20 °C and $N = 3$).

Table 2
Comparison of biosorption capacity of *X. conspersa* biomass for Hg(II) with that of different biosorbents.

Biosorbent	pH	q_m (mg g^{-1})	Reference
Chlamydomonas reinhardtii	6	72.2	[19]
Treated sawdust (*Acacia arabica*)	6	20.6	[8]
Chlamydomonas reinhardtii (Ca-alginate)	5–6	38.9	[24]
Chlamydomonas reinhardtii (immobilised-algae)	5–6	116.8	[24]
Fruit shell of *Terminalia catappa*	5–6	94.4	[25]
Wheat bran	5	70.0	[26]
Sago waste	5	55.6	[27]
Macroalga (*Cystoseira baccata*)	6	329.0	[28]
Phanerochaete chrysosporium mycelium	7	61.0	[29]
Ulva lactuca	5.5	84.7	[30]
Potamogeton natans	9–10	180.0	[31]
Cyclotella cryptica	4	11.9	[32]
Scenedesmus subspicatus	4	9.2	[32]
Camel bone charcoal	2	28.2	[33]
X. conspersa	6	82.8	This study

of both metal ions onto *X. conspersa* biomass may be carried out by chemical ion-exchange mechanism because the mean sorption energy lies within 8–16 kJ mol^{-1}.

3.6. Comparison of the biosorption capacity with that of different biosorbents

Table 2 presents the comparison of biosorption capacity of *X. conspersa* biomass for Hg(II) ions with that of different biosorbents in the literature [19,8,24–33]. As clearly seen in Table 2, the biosorption capacity of *X. conspersa* biomass for Hg(II) is higher than that of the majority of the presented biomasses. Therefore, it can be noteworthy that the *X. conspersa* biomass has important potential for the removal of Hg(II) from aqueous solution.

3.7. Desorption efficiency and reusability

The regeneration of the biosorbent is one of the key factors in assessing of its potential for commercial applications. Two different desorption agents (1 M 10 mL HCl and 1 M 10 mL HNO$_3$) were used to recover Hg(II) from the biosorbent. The best regeneration was achieved with 1 M HCl solution (10 mL) and thus it was selected as desorption agent. The desorption efficiency of Hg(II) was found to be 98%. The reusability of the biosorbent was also tested in ten consecutive sorption–desorption cycles (Fig. 8). These results showed that the natural biosorbent *X. conspersa* offers potential to be used repeatedly in Hg(II).

3.8. Biosorption kinetics

In order to clarify the biosorption kinetics of Hg(II) ions onto *X. conspersa* biomass two kinetic models, which are Lagergren's pseudo-first-order and pseudo-second-order models were applied to the experimental data. The linear form of the pseudo-first-order rate equation by Lagergren [39] is given as

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

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

The plots of $\ln(q_e - q_t)$ vs t for the pseudo-first-order model were not shown as figure due to the low R^2 values that are given in Table 3 (0.880–0.966 for 20–50 °C). It can be concluded from the R^2 values that the biosorption mechanisms of Hg(II) ions onto *X. conspersa* biomass does not follow the pseudo-first-order kinetic
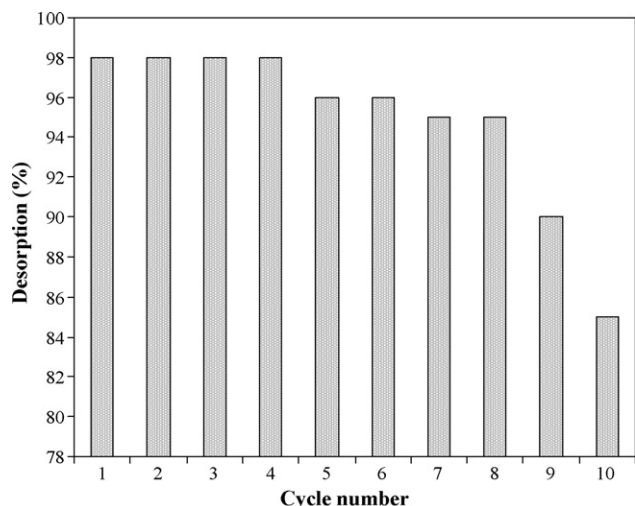
Fig. 8. Reusability of *X. conspersa* biomass with repeated sorption–desorption cycle (pH: 6, biomass concentration: 4 g/L, volume of solution: 25 mL, contact time: 60 min, initial concentration: 10 mg/L and $N = 3$).

Fig. 9. Pseudo-second-order kinetic plots at different temperatures (pH: 6, biomass concentration: 4 g/L, volume of solution: 25 mL, initial concentration: 10–400 mg/L and $N = 3$).

Fig. 10. Plot of $\ln K_D$ vs $1/T$ for the estimation of thermodynamic parameters for biosorption of Hg(II) onto *X. conspersa* biomass.

model. Moreover, from Table 3 it can be seen that the experimental values of $q_{e,\mathrm{exp}}$ are not in good agreement with the theoretical values calculated ($q_{e1,\mathrm{cal}}$) from Eq. (6). Therefore, the pseudo-first-order model is not suitable for modeling the biosorption of Hg(II) onto *X. conspersa* biomass.

Experimental data were also tested by the pseudo-second-order kinetic model which is given in the following form [40]:
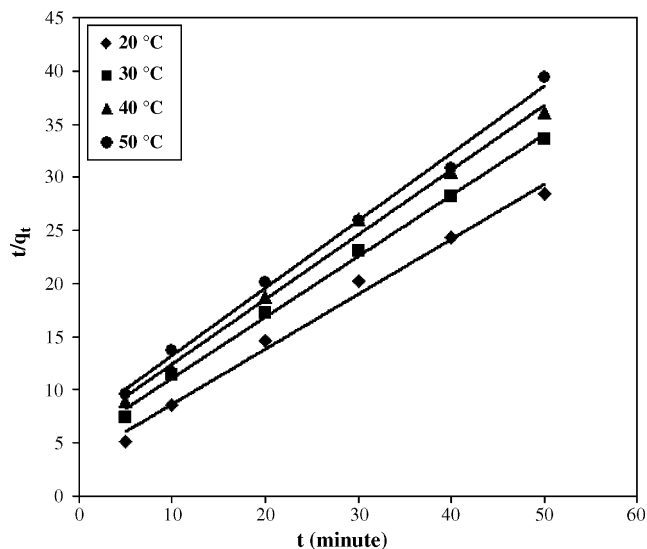
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \tag{7}$$

where k_2 (g mg^{-1} min^{-1}) is the rate constant of pseudo-second-order equation, q_t (mg g^{-1}) is the amount of biosorption time t (min) and q_e is the amount of biosorption equilibrium (mg g^{-1}).
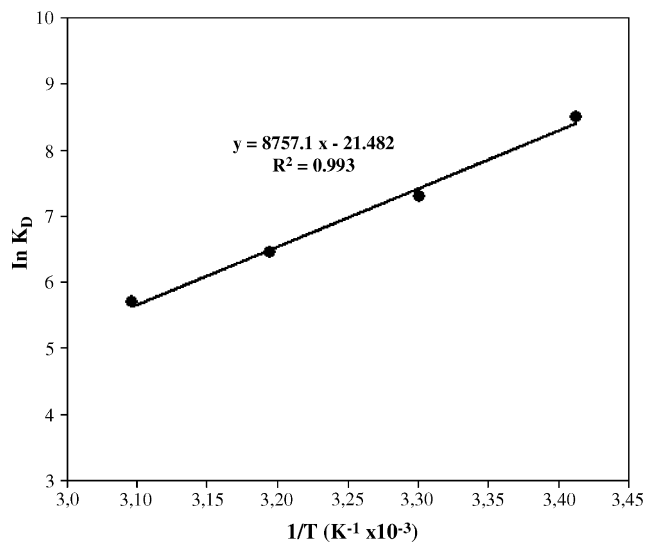
This model is more likely to predict kinetic behaviour of biosorption with chemical sorption being the rate-controlling step [41–43]. The linear plots of t/q_t vs t for the pseudo-second-order model for the biosorption of Hg(II) ions onto *X. conspersa* biomass at 20–50 °C were shown in Fig. 9. The rate constant (k_2), the R^2 and q_e values are given in Table 3. It is clear from these results that the R^2 values are very high (in range of 0.991–0.997) for Hg(II) biosorption. In addition, the theoretical $q_{e2,\mathrm{cal}}$ values were closer to the experimental $q_{e,\mathrm{exp}}$ values (Table 3). In the view of these results, it can be said that the pseudo-second-order kinetic model provided a good correlation for the biosorption of Hg(II) onto *X. conspersa* biomass in contrast to the pseudo-first-order model.

3.9. Biosorption thermodynamics

Thermodynamic behaviour of the biosorption of Hg(II) ions onto *X. conspersa* biomass was investigated using the thermodynamic parameters that include the change in free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o). These parameters were calculated from following equation:

$$\Delta G^o = -RT \ln K_D \tag{8}$$

where, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is temperature (K) and K_D (q_e/C_e) is the distribution coefficient.

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

$$\ln K_D = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{9}$$

Table 3
Kinetic parameters obtained from pseudo-first-order and pseudo-second-order models for Hg(II) onto *X. conspersa* biomass at different temperatures.

Temperature (°C)	$q_{e,\mathrm{exp}}$ (mg g^{-1})	Pseudo-first-order			Pseudo-second-order		
		k_1 (min^{-1})	$q_{e1,\mathrm{cal}}$ (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	$q_{e2,\mathrm{cal}}$ (mg g^{-1})	R^2
20	1.82	4.8×10^{-2}	1.20	0.961	7.8×10^{-2}	1.93	0.991
30	1.65	4.5×10^{-2}	1.17	0.908	6.2×10^{-2}	1.74	0.997
40	1.56	4.4×10^{-2}	1.10	0.880	5.9×10^{-2}	1.64	0.995
50	1.47	4.3×10^{-2}	1.06	0.966	5.8×10^{-2}	1.58	0.995

Based on Eq. (9), the ΔH^o and ΔS^o parameters can be calculated from the slope and intercept of the plot of $\ln K_D$ vs $1/T$, respectively (Fig. 10).

Gibbs free energy change (ΔG^o) was calculated to be −20.7, −18.4, −16.8, and −15.3 kJ mol^{-1} for Hg(II) biosorption. The negative ΔG^o values indicated thermodynamically feasible and spontaneous nature of the biosorption. The decrease in ΔG^o values with increase in temperature shows a decrease in feasibility of biosorption at higher temperatures. The ΔH^o parameter was found to be −72.8 kJ mol^{-1}. The negative ΔH^o indicates the exothermic nature of the biosorption process of Hg(II) at 20–50 °C. The ΔS^o parameter was found to be −178.6 J mol^{-1} K^{-1}. The negative ΔS^o value suggests a decrease in the randomness at the solid/solution interface during the biosorption process of Hg(II).

4. Conclusions

In this study, the use of *X. conspersa* as a natural biosorbent was tested for removing Hg(II) ions from aqueous solution. The batch study parameters, pH of solution, biomass concentration, contact time, and temperature, were found to be effective on the biosorption efficiency of Hg(II).

The biosorption capacity of *X. conspersa* biomass was determined as 82.8 mg g^{-1} Hg(II) at optimum conditions of pH 6, biomass concentration of 4 g/L, contact time of 60 min and solution temperature of 20 °C. The mean free energy values evaluated from the D–R model indicated that the biosorption of Hg(II) onto *X. conspersa* biomass was taken place by chemical ion-exchange. The FT-IR spectroscopic analysis confirmed that the functional groups on the biosorbent surface were involved in Hg(II) biosorption. The kinetic studies revealed that the biosorption process followed well the pseudo-second-order kinetic model. The calculated thermodynamic parameters showed the feasibility, exothermic and spontaneous nature of the biosorption of Hg(II) ion onto *X. conspersa* biomass. The recovery tests indicated that 1 M HNO$_3$ solution was able to elute 95% of Hg(II) from the biomass. The reusability of the biosorbent was good after six consecutive sorption–desorption cycles. Based on all results, the *X. conspersa* biomass as a natural and low-cost biomass can be used as alternative biosorbent for the treatment of wastewaters containing Hg(II) ions.

Acknowledgements

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