Removal of mercury(II) from aqueous solution using moss (*Drepanocladus revolvens*) biomass: Equilibrium, thermodynamic and kinetic studies

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ARTICLE INFO

ABSTRACT

The equilibrium, thermodynamics and kinetics of the biosorption of Hg(II) onto moss (*Drepanocladus revolvens*) biomass from aqueous solution were investigated. Optimum experimental parameters were determined to be pH 5.5, contact time 60 min, biomass concentration $4\,g\,L^{-1}$ of solution, and temperature $20\,°C$. From the Langmuir model the maximum biosorption capacity of the moss biomass was found to be $94.4\,mg\,g^{-1}$. The mean free energy value ($10.2\,kJ\,mol^{-1}$) evaluated by using the Dubinin–Radushkevich (D–R) model indicated that the biosorption of mercury ions onto *D. revolvens* was taken place by chemical ion-exchange. The kinetic studies indicated that the biosorption process of mercury ions followed well pseudo-second-order model. The calculated thermodynamic parameters ($\Delta G°$, $\Delta S°$, $\Delta H°$) showed the biosorption to be exothermic and spontaneous with decreased randomness at the solid–solution interface. The recovery of the Hg(II) from *D. revolvens* biomass was found to be 99% using 1 M HCl. It was concluded that the *D. revolvens* biomass can be used as biosorbent for the treatment of wastewaters containing Hg(II) ions.

1. Introduction

Heavy metals are released continuously from different sources, industrial, agricultural and domestic wastes into the environment, which create problem for human as well as aquatic organisms. The pollution of water resources due to the indiscriminate disposal of heavy metals has been causing worldwide concern for the last few decades. It is well known that some metals can have poisonous or harmful effects on many forms of life [1].

Mercury is one of the most toxic heavy metals released in the environment and readily accumulated by organisms [2,3]. Mercury has very high tendency for binding to proteins and it mainly affects the renal and nervous systems [4]. In humans, the initial symptoms include numbness of the lips and limbs. As the sickness progresses, permanent damage is done to the central nervous system, and the victim experiences visual constriction, loss of motor coordination, and, in the final stages prior to death, loss of memory, speech, hearing, and taste. In addition, mercury is easily absorbed through skin, respiratory, and astrointestinal tissues [5]. 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 [6]. In addition, this heavy 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 [7]. The European Union considers mercury as a priority and hazardous pollutant and defines a maximum permissible concentration of total mercury as low as $1\,\mu g\,L^{-1}$ for drinking water and $5\,\mu g\,L^{-1}$ for wastewater discharge [8]. 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 [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, preconcentration, reverse osmosis, evaporation, membrane filtration, adsorption and biosorption [10]. These processes are expensive, and also have other shortcomings, such as incomplete removal of metals, limited tolerance to pH change, moderate or no metal selectivity, very high or low working levels of heavy metals, and production of toxic sludge or other waste products that also need disposal [11]. Hence, environmental and public health engineers have been searching for an inexpensive and efficient technology for the treatment of metal-containing wastes. The use of biosorption to remove heavy metals is one of such technology that has received considerable attention in the past two decades [12]. This method plays an important role in the elimination of heavy metal ions from aqueous solutions in water pollution control [13]. The main advantages of this technique are the reusability of biomaterial, low operating cost, improved

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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 [14]. Various biomasses have been used for the removal of Hg(II) ions from aqueous solution [15,16].

Mosses are cryptogamic organisms which occur in almost all terrestrial ecosystems and by virtue of their ability to tolerate long periods of drought may even colonize areas with extreme environmental conditions [17]. They have been used for more than 20 years as biomonitors for the determination of atmospheric heavy metal deposition because of their high cation exchange capacity [18,19]. Different kinds of mosses have also been used for removing different heavy metals from aqueous solution [20–23]. *D. revolvens* is marked by its long, tapered leaves, which are strongly curled around to the extent of almost forming a circle. The leaves are orientated to one side of the stem. It is a robust plant and is usually tinged with orange, crimson or purple, mixed with yellowish-green. This moss species is a natural and readily available and considered as low-cost biomass.

In this study, the biosorption potential of the *D. revolvens* biomass to remove Hg(II) from aqueous solution was investigated using 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) onto *D. revolvens* biomass were also evaluated in terms of thermodynamics and kinetics.

2. Experimental

2.1. Biomass preparation

The moss biomass (*D. revolvens*) sample was collected from the East Black Sea coast of Turkey. Samples were washed with deionized water and inactivated by heating in an oven at 70 °C for 48 h. The inactivated dried moss 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 supplied from Sigma (St. Loius, MO, USA). Double deionized 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 ($H_2PO_4^-/H_3PO_4$) were prepared by mixing of appropriate volumes of 1 mol L^{-1} sodium dihydrogen phosphate and phosphoric acid solutions at pH 2. Acetate buffer solutions (CH_3COO^-/CH_3COOH) were prepared by mixing of appropriate volumes of 1 mol L^{-1} acetic acid and 1 mol L^{-1} sodium acetate solutions at pH 4. Phosphate buffer solutions ($H_2PO_4^-/HPO_4^{2-}$) were prepared by mixing of appropriate volumes of 1 mol L^{-1} sodium dihydrogen phosphate and 1 mol L^{-1} sodium hydrogen phosphate at pH 5 and 6. Ammonium buffer solutions were prepared by mixing of appropriate amounts of 1 mol L^{-1} ammonia and 1 mol L^{-1} ammonium chloride solutions at pH 8.

Perkin Elmer Analyst 700 (Norwalk, CT, USA) 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. NaBH$_4$ (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^{-1} stock solution of Hg(II) was prepared by HgCl$_2$ (E. Merck, Darmstadt, Germany). Biosorption experiments were conducted using the solutions having 10 mg L^{-1} of Hg(II) with the optimum biomass concentration, 4 g L^{-1}.

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^{-1}), contact time (5–120 min), pH (2–8), biomass concentration (0.4–16 g L^{-1}), 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 filters (Double rings, China). The metal concentration of filtrate was analyzed using CVAAS. Each determination was replicated three times and the mean results were considered in the analysis. The percent biosorption of the metal ion was calculated as follows:

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

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 were carried out by using 1 M HNO$_3$ (10 mL) and 1 M HCl (10 mL). After determination of metal contents 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.

3. Results and discussion

3.1. FT-IR analysis

The FT-IR spectroscopy method was used to obtain information on the nature of possible biosorbent–metal ions interactions. Fig. 1 shows the FT-IR spectra of unloaded and Hg(II)-loaded biomass samples. The FT-IR spectra of the moss biomass indicate the pres-
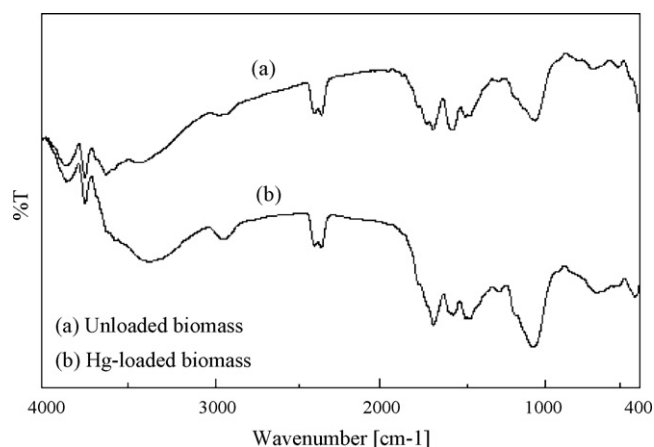

Fig. 1. FT-IR spectrum of unloaded and Hg(II)-loaded biomass.

ence of amino, carboxylic, hydroxyl and carbonyl groups. The broad bands at 3855, 3740, 3613, and 3404 cm^{-1} are dominated by –OH and –NH stretching. The peaks at 2319 and 2362 cm^{-1} represent stretching vibrations of –NH$_2^+$, –NH$^+$ and –NH groups of the moss biomass. The peaks at 2912, 1426, and 1455 cm^{-1} representing C–H stretching vibrations, N–H bending, –CH$_3$ wagging vibrations, respectively, are due to the several functional groups present on the cell surfaces of the moss biomass. The peaks at 1645, 1681, and 1735 cm^{-1} are caused by the stretching band of carboxyl (–C=O) groups. The bands observed at 1034 and 1152 cm^{-1} were assigned to P–O alkyl (phosphorous compounds) stretching (stretching vibrations). The peaks at 784, 682, and 532 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 moss biomass compared with that of the unloaded moss biomass. The bands observed at 3855, 3740 and 3404 cm^{-1} were shifted to 3846, 3738 and 3352 cm^{-1}, respectively. The peaks at 2319 and 2362 cm^{-1} were changed to 2315 and 2357 cm^{-1}, respectively. The peak stretching band of carboxyl (–C=O) groups was shifted from 1645 to 1643 cm^{-1}. The stretching bands observed at 1034 and 1152 cm^{-1} were shifted to 1043 and 1155 cm^{-1}, respectively. The peaks at 784 and 532 cm^{-1} are also shifted to 772 and 522 cm^{-1}. The analysis of the FT-IR spectral results showed that the functional groups (carboxyl –COOH, hydroxyl –OH, amine –NH$_2$, and phosphor P–O) are responsible for the binding of Hg(II) ions to cell surfaces of the moss biomass. The same mechanism was reported for the biosorption of Cd(II) and Zn(II) ions on aquatic moss, *Fontinalis antipyretica* [24]. It was reported in another study that the same functional groups of terrestrial moss, *Pleurozium schreberi* was responsible for metal-binding capacity [25]. Moreover, the parallel results were reported for the biosorption of Hg(II) by algae and fungi biomasses which have the same functional groups [26,27].

3.2. Effect of pH

The pH parameter has been identified as one of the most important parameter that is effective on metal sorption. It is directly related with competition ability of hydrogen ions with metal ions to active sites on the biosorbent surface [28]. The effect of pH on the biosorption of Hg(II) ions onto *D. revolvens* biomass was studied by changing pH values in range of 2–8 and the results were presented in Fig. 2. The biosorption efficiency was increased from 70% to 91.5% as pH was increased from 2 to 5. The maximum biosorption was found to be 96% at pH 5.5. Therefore, the remaining all biosorption experiments were carried out at this pH value.

The biosorption mechanism on the biomass surface reflects the nature of the physicochemical interaction of the species in solution and the biosorptive sites of sorbent [29,30]. At low pH value (pH 2), 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 competing with metal ions for the sorption sites. The increase in biosorption in the pH range 2–5.5 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 (5.5–8), the decrease in biosorption is due to the formation of soluble hydroxilated compound (Hg(OH)$_2$). The maximum Hg(II) removal was found to be 97% at pH 5.5 and therefore the biosorption experiments were carried out at this pH value. Several authors have reported maximum biosorption of mercury by different biomasses at pH 5.5 or near values [30–33].
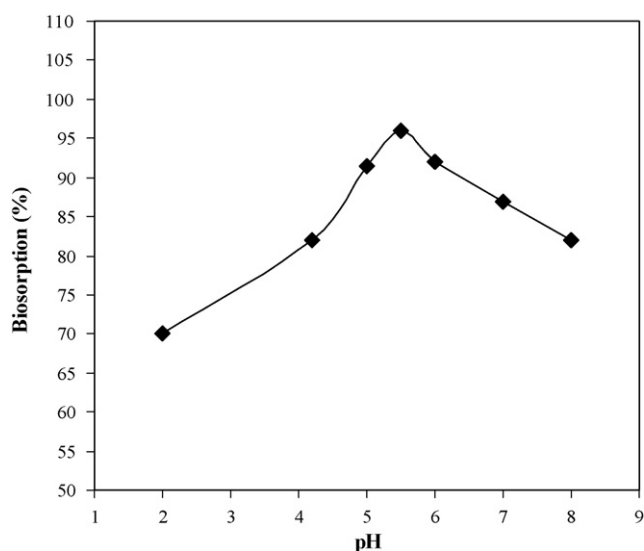

Fig. 2. Effect of pH on the biosorption of Hg(II) onto *D. revolvens* biomass (biomass concentration: 4 g L^{-1}; volume of solution: 25 mL; initial concentration: 10 mg L^{-1}; contact time: 60 min; temperature: 20 °C).

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 biosorption steeply increases with raising the biomass concentration from 0.4 to 4 g L^{-1}. This is because of the availability of more binding sites and thus making easier penetration of Hg(II) ions to the sorption sites. The maximum biosorption was found to be 97% as biomass concentration was 4 g L^{-1}. Further increment in the biomass concentration did not cause significant improvement in biosorption capacity. This may be due to the binding of almost all ions to the sorbent and the establishment of equilibrium between the ions bound to the sorbent and those remaining unsorbed in the solution [34]. Therefore, the optimal biomass concentration was selected as 4 g L^{-1} for the further experiments.
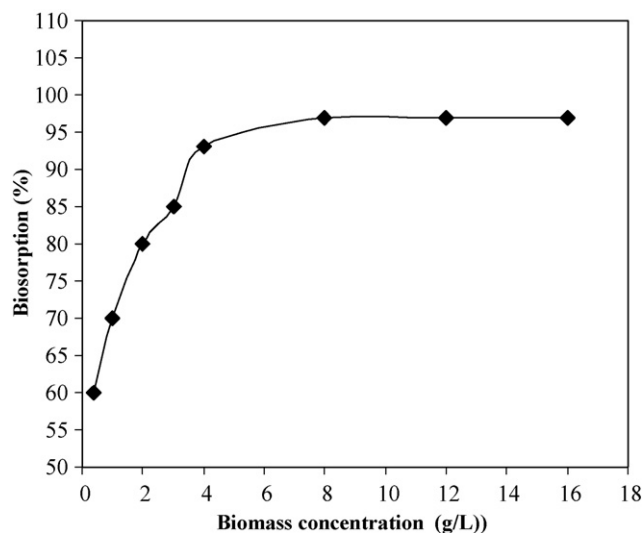

Fig. 3. Effect of biomass concentration on the biosorption of Hg(II) onto *D. revolvens* biomass (pH: 5.5; volume of solution: 25 mL; initial concentration: 10 mg L^{-1}; temperature: 20 °C).

3.4. Effects of contact time and temperature

Contact time is one of the most important parameters for successful usage of the biosorbents in practical and rapid sorption application [35,36]. Fig. 4 shows the effect of contact time on the biosorption of Hg(II) ions onto *D. revolvens*. 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.

The temperature of the biosorption medium could be important for energy dependent mechanisms in metal biosorption by microorganisms. Energy independent mechanisms are less likely to be affected by temperature since the process responsible for biosorption is largely physicochemical in nature [27]. Therefore, experiments were performed to examine the temperature effect on the biosorption yield of Hg(II) by *D. revolvens* and the results are given in Fig. 4. The percentage removal decreased from 98% to 82% as temperature was increased from 20 to 50 °C at the equilibrium time, 90 min. The observed trend with increasing temperature suggests that biosorption process of mercury by the moss 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 [37]:
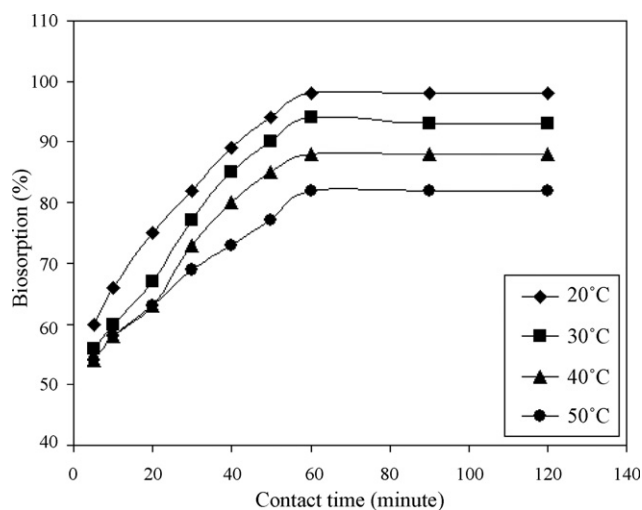
$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2}$$

Fig. 4. Effect of contact time and temperature on the biosorption of Hg(II) onto *D. revolvens* biomass (pH: 5.5; biomass concentration: $4\,\mathrm{g\,L^{-1}}$; volume of solution: 25 mL; initial concentration: $10\,\mathrm{mg\,L^{-1}}$).

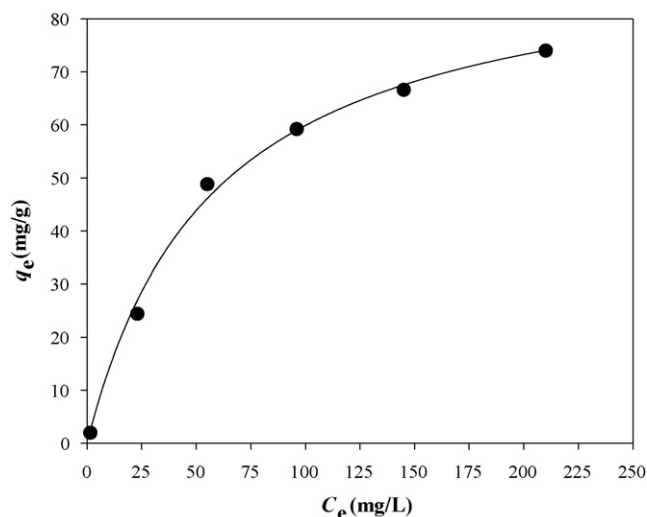**Fig. 5.** Langmuir isotherm plots for the biosorption of Hg(II) onto *D. revolvens* biomass (pH: 5.5, biomass concentration: $4\,\mathrm{g\,L^{-1}}$; volume of solution: 25 mL; initial concentration: 10–$400\,\mathrm{mg\,L^{-1}}$; contact time: 60 min; temperature: 20 °C).

where q_e is the equilibrium metal ion concentration on the sorbent $(\mathrm{mg\,g^{-1}})$, C_e is the equilibrium metal ion concentration in the solution $(\mathrm{mg\,L^{-1}})$, q_m is the monolayer sorption capacity of the sorbent $(\mathrm{mg\,g^{-1}})$, and K_L is the Langmuir sorption constant $(\mathrm{L\,mg^{-1}})$ 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 *D. revolvens* biomass against the concentration of Hg(II) ions remaining in the solution $(\mathrm{mg\,L^{-1}})$. The coefficients of determination (R^2) were found to be 0.996, indicating that the biosorption of Hg(II) onto *D. revolvens* biomass fitted well the Langmuir model. In other words, the sorption of Hg(II) ions onto *D. revolvens* was taken place at the functional groups/binding sites on the surface of the biomass which is regarded as monolayer biosorption.

The maximum biosorption capacity (q_m) of *D. revolvens* biomass for mercury ions was found to be $94.4\,\mathrm{mg\,g^{-1}}$. The K_L value was also found as $0.017\,\mathrm{L\,mg^{-1}}$. In addition, Table 1 presents the comparison of biosorption capacity of *D. revolvens* biomass for Hg(II) ions with that of different biosorbents in literature [3,26,27,31–33,38–45]. As clearly seen in Table 1, the biosorption capacity of *D. revolvens* biomass for Hg(II) is higher than that of the majority of the

Table 1
Comparison of biosorption capacity of *D. revolvens* biomass for Hg(II) with that of different biosorbents.

| Biosorbent	pH	q_m $(\mathrm{mg\,g^{-1}})$	Reference
Eucalyptus *camaldulensis* bark	8–10	33.1	[3]
Chlamydomonas reinhardtii	6	72.2	[26]
Aspergillus niger	3	40.5	[27]
Treated sawdust (*Acacia arabica*)	6	20.6	[30]
Chlamydomonas reinhardtii (Ca-alginate)	5–6	38.9	[31]
Chlamydomonas reinhardtii (immobilized-algae)	5–6	116.8	[31]
Fruit shell of *Terminalia catappa*	5–6	94.4	[32]
Ulva lactuca	5.5	84.7	[33]
Wheat bran	5	70.0	[38]
Sago waste	5	55.6	[39]
Macroalga (*Cystoseira baccata*)	6	329.0	[40]
Phanerochaete chrysosporium mycelium	7	61.0	[41]
Potamogeton natans	9–10	180.0	[42]
Cyclotella cryptica	4	11.9	[43]
Scenedesmus subspicatus	4	9.2	[43]
Camel bone charcoal	2	28.2	[44]
Pyrolyzed sewage sludge	5	175.4	[45]
Chemical activated sewage sludge	5	64.9	[45]
D. revolvens	5.5	94.4	This study
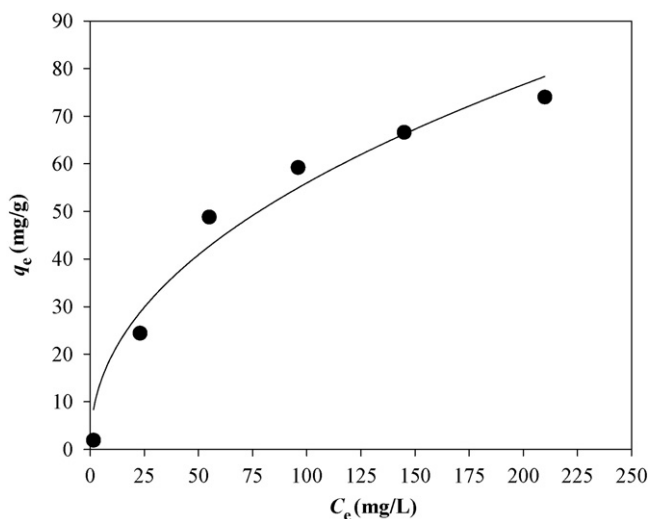
Fig. 6. Freundlich isotherm plots for the biosorption of Hg(II) onto *D. revolvens* biomass (pH: 5.5, biomass concentration: $4\,g\,L^{-1}$; volume of solution: 25 mL; initial concentration: 10–$400\,mg\,L^{-1}$; contact time: 60 min; temperature: 20 °C).

presented biomasses. Therefore, it can be noteworthy that the *D. revolvens* biomass has important potential for the removal of Hg(II) from aqueous solution.

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 [46] is

$$q_e = K_f C_e^{1/n} \qquad (3)$$

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 *D. revolvens* biomass. The values of K_f and $1/n$ were found to be 6.95 and 0.45 Hg(II) biosorption, respectively. The $1/n$ values were between 0 and 1 indicating that the biosorption of Hg(II) was favorable at studied conditions. However, the R^2 values were found to be 0.964, indicating that this model was not able to adequately describe the relationship between the amounts of sorbed mercury ions and their equilibrium concentration in the solution. Therefore, it can be concluded that the Langmuir isotherm model best fitted the equilibrium data since it presents higher R^2 values.

The equilibrium data were also subjected to the D–R isotherm model to determine the nature of biosorption process of Hg(II) onto *D. revolvens* as physical or chemical and the results were shown in Fig. 7. The linear form of the D–R isotherm equation [47] is

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \qquad (4)$$

where q_e is the amount of metal ions sorbed on per unit weight of biomass ($mol\,g^{-1}$), q_m is the maximum biosorption 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 isotherm model well fitted the equilibrium data since the R^2 value was found as high as 0.993. The q_m value was found using the intercept of the plots to be $1.44 \times 10^{-3}\,mol\,g^{-1}$.

The mean free energy (E, $kJ\,mol^{-1}$) is calculated by using the β value [48]:

$$E = \frac{1}{\sqrt{-2\beta}} \qquad (5)$$
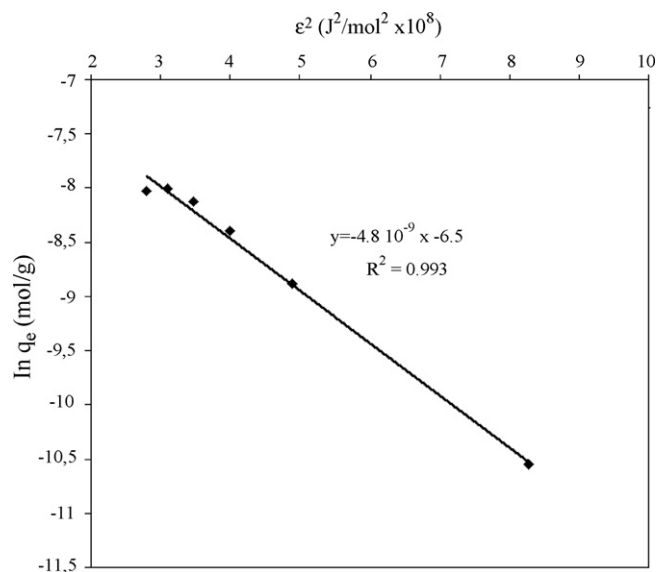

Fig. 7. D–R isotherm plots for the biosorption of Hg(II) onto *D. revolvens* biomass (pH: 5.5; biomass concentration: $4\,g\,L^{-1}$; contact time: 60 min; initial concentration: 10–$400\,mg\,L^{-1}$; contact time: 60 min; temperature: 20 °C).

The E ($kJ\,mol^{-1}$) value gives information about sorption mechanism, physical or chemical. If it lies between 8 and $16\,kJ\,mol^{-1}$, the sorption process takes place chemically, while, $E < 8\,kJ\,mol^{-1}$, the sorption process proceeds physically [49,50]. The mean biosorption energy was calculated to be $10.2\,kJ\,mol^{-1}$. This result suggests that the biosorption process of mercury ions onto *D. revolvens* biomass may be carried out by chemical ion-exchange mechanism because the mean sorption energy lies within 8–$16\,kJ\,mol^{-1}$.

3.6. 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 desorbe the Hg(II) from the biosorbent. The desorption efficiency of Hg(II) was found to be 99% and 60% using 1 M HCL and 1 M HNO$_3$, respectively. Therefore, 1 M HCl solution (10 mL) was selected as desorption agent. The reusability of the biosorbent was also tested in ten consecutive sorption–desorption cycles (Fig. 8). These results showed that the natural biosorbent *D. revolvens* offers potential to be used repeatedly in Hg(II).

3.7. Biosorption kinetics

In order to clarify the biosorption kinetics of Hg(II) ions onto *D. revolvens* biomass two kinetic models, which are Lagergren's pseudo-first-order and pseudo-second-order model were applied to the experimental data. The linear form of the pseudo-first-order rate equation by Lagergren [51] is given as

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (6)$$

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 constants (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 2 (0.882–0.958 for 20–50 °C). It can be concluded from the R^2 values that the biosorption mechanisms of Hg(II) ions onto *D. revolvens* biomass does not follow the pseudo-first-order kinetic
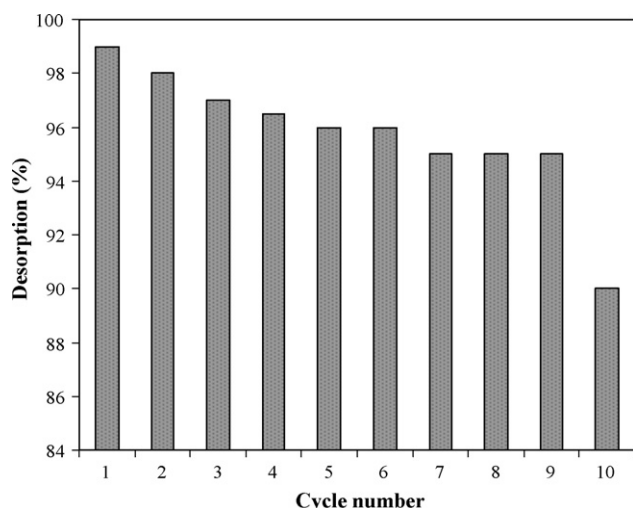
Fig. 8. Reuseability of *D. revolvens* biomass with repeated sorption–desorption cycle (pH: 5.5, biomass concentration: $4\,g\,L^{-1}$; volume of solution: 25 mL; contact time: 60 min; initial concentration: $10\,mg\,L^{-1}$).
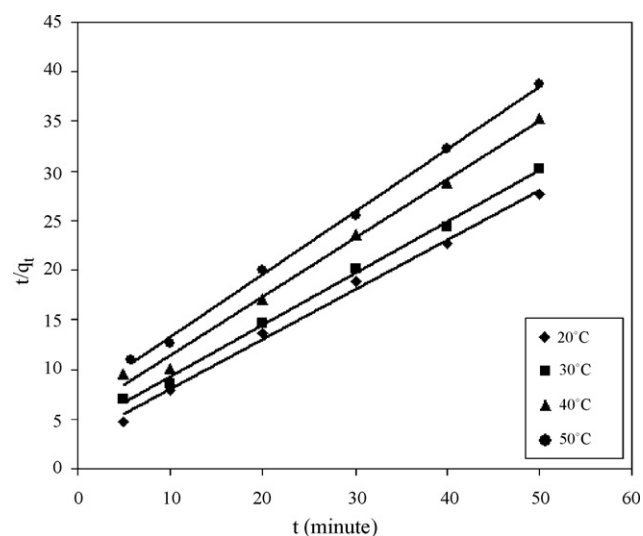

Fig. 9. Pseudo-second-order kinetic plots at different temperatures (pH: 5.5, biomass concentration: $4\,g\,L^{-1}$; volume of solution: 25 mL; initial concentration: $10–400\,mg\,L^{-1}$).

model. Moreover, from Table 2 it can be seen that the experimental values of $q_{e,exp}$ are not in good agreement with the theoretical values calculated ($q_{e1,cal}$) from Eq. (6). Therefore, the pseudo-first-order model is not suitable for modeling the biosorption of Hg(II) onto *D. revolvens* biomass.

Experimental data were also tested by the pseudo-second-order kinetic model which is given in the following form [52]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \qquad (7)$$

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 behavior of biosorption with chemical sorption being the rate-controlling step [53]. The linear plots of t/qt vs t for the pseudo-second-order model for the biosorption of Hg(II) ions onto *D. revolvens* biomass at 20–50 °C were shown in Fig. 9. The rate constants (k_2), the R^2 and q_e values are given in Table 2. It is clear from these results that the R^2 values are very high (in range of 0.993–0.998). In addition, the theoretical $q_{e2,cal}$ values were closer to the experimental $q_{e,exp}$ values. 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 *D. revolvens* biomass in contrast to the pseudo-first-order model.

3.8. Biosorption thermodynamics

Thermodynamic behavior of the biosorption of Hg(II) ions onto *D. revolvens* biomass was investigated using the thermodynamic parameters that include the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°). These parameters were calculated from

the following equations:

$$\Delta G^{\circ} = -RT \ln K_D \qquad (8)$$

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

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

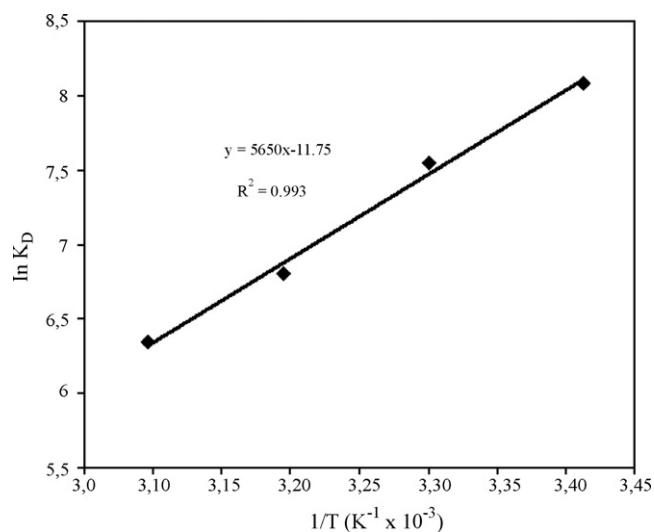$$\ln K_D = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \qquad (9)$$

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

Table 2
Kinetic parameters obtained from pseudo-first-order and pseudo-second-order for the of Hg(II) onto *D. revolvens* biomass at different temperatures.

Temperature (°C)	Pseudo-first-order			Pseudo-second-order			
	$q_{e,exp}$ ($mg\,g^{-1}$)	k_1 (min^{-1})	$q_{e1,cal}$ ($mg\,g^{-1}$)	R^2	k_2 ($g\,mg^{-1}\,min^{-1}$)	$q_{e2,cal}$ ($mg\,g^{-1}$)	R^2
20	1.94	5.4×10^{-2}	1.33	0.939	8.6×10^{-2}	1.99	0.995
30	1.85	5.0×10^{-2}	1.18	0.958	6.8×10^{-2}	1.92	0.997
40	1.76	3.9×10^{-2}	1.16	0.945	6.4×10^{-2}	1.70	0.993
50	1.62	3.8×10^{-2}	1.07	0.882	5.8×10^{-2}	1.59	0.998

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

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

4. Conclusions

Trace elements play important negative and positive roles in human life [54–56]. In this study, the use of *D. revolvens* as a natural biosorbent was tested for removing of 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 *D. revolvens* biomass was determined as $94.4 \, \text{mg g}^{-1}$ Hg(II) at optimum conditions of pH 5.5, biomass concentration of $4 \, \text{g L}^{-1}$, 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 *D. revolvens* biomass was taken place by chemical ion-exchange. The FT-IR spectroscopic analysis confirmed that 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 *D. revolvens* biomass. The recovery tests indicated that 1 M HCl solution was able to elute 99% of Hg(II) from the biomass. The reusability of the biosorbent was good after six consecutive sorption–desorption cycles. Based on all results, the *D. revolvens* biomass can be used as alternative biosorbent for the treatment of wastewaters containing Hg(II) ions because of advantages of being natural, low-cost biomass and having high biosorption capacity, reasonably rapid biosorption rate and good reusability after ten biosorption–desorption cycles without any considerable loss of biosorption capacity.

Acknowledgements

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