Sequestration of Pb(II) and Ni(II) ions from aqueous solution using microalga *Rhizoclonium hookeri*: adsorption thermodynamics, kinetics, and equilibrium studies

S. Suganya, A. Saravanan, P. Senthil Kumar, M. Yashwanthraj, P. Sundar Rajan and K. Kayalvizhi

ABSTRACT

In the present study, the microalga *Rhizoclonium hookeri* (RH) was effectively applied to remove the metal ions [Pb(II) and Ni(II)] from aqueous solution in batch adsorption mode experiments. The adsorption process was influenced by several operating parameters such as initial metal ion concentration, contact time, pH, particle size, adsorbent dose, and temperature. The maximum monolayer adsorption capacity of the RH was found to be 81.7 mg g^{-1} and 65.81 mg g^{-1} for Pb(II) and Ni(II) ions, respectively, at optimum conditions. The calculated thermodynamic parameters illustrated that the adsorption process was found to be spontaneous and endothermic in nature. Experimental data were analyzed in terms of pseudo-first order, pseudo-second order, and Elovich kinetic models. The results showed that the removal of Pb(II) and Ni(II) ions followed the pseudo-second order kinetics. The adsorption isotherm data were described using two and three parameter models. The results indicate that the adsorption data were best fitted with the Sips isotherm model. Consequently, the microalga RH with good adsorbability and reusability could be used as an effective adsorbent for the adsorption of Pb(II) and Ni(II) ions from wastewater.

Key words | biosorption, kinetic parameters, modeling, *Rhizoclonium hookeri*, separation, wastewater treatment

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INTRODUCTION

Industrial and domestic wastewater has become a serious threat to water resources around the world. This wastewater mostly contains hazardous chemicals, such as heavy metals and organic toxicants which are persistent and gradually accumulate in food chains and can cause irreparable damage to people and the environment (Xu *et al.* 2014). Among the heavy metals, Pb(II) and Ni(II) are considered to be major toxic pollutant for water bodies even at very low concentrations. The maximum permissible limit for Pb(II) and Ni(II) ions in drinking water has been fixed at 0.01 and 0.02 mg/L (Bureau of Indian Standards 2009). These metal ions are mostly released in excess amount from industries such as electroplating, metal finishing, porcelain enameling, paint and dyes, vegetable fat producing industries, lead batteries, electroplating, mining and smelters as well as other industrial, urban, and agricultural activities (Anbalagan *et al.* 2015). Bioaccumulation of these metals may cause long-term health hazards such as skin allergies, lung fluorosis, cyanosis, nausea and vomiting, different degrees of poisoning to the kidney, and also affects the cardiovascular system, liver, central nervous system, and gastrointestinal system (Fu *et al.* 2015). Hence, the removal of these heavy metals has

become a major concern for researchers in recent years. Several conventional methods have been employed for the removal of Pb(II) and Ni(II) from aqueous solution, such as chemical precipitation (Purkayastha *et al.* 2014), membrane separation (Alzahrani & Mohammad 2014), ion exchange (Fu & Wang 2011), reverse osmosis (Bhattacharya *et al.* 2013), electrodialysis (Slesarenko 2003), and electrochemical treatment (Tran *et al.* 2012). However, these methods are restricted due to their own demerits such as high cost, complexity, low efficiency, or waste disposal. Hence, researchers turned their attention towards adsorption technology, which is recognized to be an efficient method for the removal of these heavy metals from aqueous solution. This adsorption can be done with various adsorbents, such as polymers (Gao *et al.* 2014), clay minerals (Lee & Tiwari 2012), oxides (Minju *et al.* 2015), carbon materials (Yang & Jiang 2014), and biosorbents (Dong *et al.* 2014). Among these, biosorbents seem to be very efficient for removal of heavy metals with low concentration and inexpensive material, fast metal recovery, and regeneration. Mostly, waste biomass has been used as a biosorbent, and mainly consists of various functional groups such as alcohol, aldehydes, ketones, carboxylic, ether, and phenol. These functional groups play a vital role in binding the heavy metals towards the surface of the biosorbents. To date, several studies on the potential of biosorbents such as non-living biomass (e.g., bark, lignin, shrimp, krill, squid, crab shell, etc.), microbial biomass (e.g., bacteria, fungi, yeasts), and algal biomass have been tested for removal of different heavy metals present in synthetic and field wastewater (Vijayaraghavan & Prabu 2006; Singh *et al.* 2008; Vilar *et al.* 2008; Rajfur *et al.* 2012). Algae are a renewable natural biomass found abundantly all over the world because they have the capability to survive in dual environment conditions such as in fresh and marine brackish water. They also have several attractive features, such as low cost, excellent reusability, high metal sorption capacity, and CO_2 sequestration. In these respects, algae have been used as an effective biosorbent material for the sorption of heavy metals. In this study, algal biomass, *Rhizoclonium hookeri* (RH), was used as an effective biosorbent for the removal of Pb(II) and Ni(II) from wastewater. This species has the aforementioned biosorption properties and, in addition, it also has high mechanical stability to adapt to extreme conditions during the regeneration process.

MATERIALS AND METHODS

Chemicals and equipment

The chemicals lead(II) nitrate [Pb(NO$_3$)$_2$] and nickel(II) sulfate hexahydrate [NiSO$_4$.6H$_2$O] of analytical reagent grade were received from Rankem Fine Chemicals Limited, India. The pH of the wastewater was adjusted by using 0.1 N HCL and 0.1 N NaOH and the pH was measured using a pH meter (Elico Limited, India). The concentration of Pb(II) and Ni(II) ions were observed using an atomic adsorption spectrophotometer (AAS) (SL 176 Model, Elico Limited, Chennai, India).

Collection and preparation of the adsorbents

In this research, RH was used as an effective adsorbent for the adsorption of metal ions. The microalgae RH was collected from various ponds, wells, and other pools of water available near Dharmapuri, Tamilnadu, India (Kayalvizhi *et al.* 2015). These were washed with water two to three times to remove the impurities and debris materials present on the surface of the algae. After washing the samples were allowed to dry in sunlight for about 10 days to completely remove the moisture content. These dried samples were ground to a fine powder and then collected in a porcelain dish for acid treatment. 0.1 M hydrochloric acid (HCl) was added to the sample where it remained for about 5 hours in an orbital shaker with a speed of 150 rpm. After this the adsorbent material was washed with distilled water to remove the excess amount of HCl present in it. It was washed until the pH of the water became neutral. Then the adsorbent was allowed to dry for about 24 hours at 60 °C in a hot air oven. The resultant material was collected in a plastic container and used as an adsorbent material for the effective removal of Pb(II) and Ni(II) ions.

Batch adsorption studies

Batch adsorption studies were carried out to obtain the removal of the metal ions from the aqueous solution. The studies were carried out in a 250 mL Erlenmeyer flask and the studies were performed in a temperature controlled

incubation shaker at 150 rpm. The experiments were carried out by changing the various parameters, such as contact time, temperature, pH, adsorbent dosage, and initial metal ion concentration. In a 250 mL Erlenmeyer flash, the desired concentration of aqueous solution was used and the required quantity of adsorbent was weighed and added to it. The contact time was varied and the temperature was changed by using a temperature controlled incubation shaker. Also, the pH of the aqueous solution could be varied by adding 0.1 M NaOH or 0.1 M HCl. On reaching the desired contact time, the Erlenmeyer flasks were taken out from the shaker and the solution was filtered using a 0.45 μm Whatman filter paper. Then the supernatants were collected and the metal ion concentration was analyzed using an AAS. The concentrations of metal ions was calculated using the following formula:

$$\% \text{ Removal of metal ions} = \frac{C_o - C_e}{C_o} \times 100 \tag{1}$$

where C_o and C_e are the initial and final concentrations (mg L^{-1}) of metal ions, respectively.

Adsorption equilibrium experiments

The adsorption equilibrium experiments were performed in 250 mL Erlenmeyer flasks with 100 mL metal ion solutions with an initial metal ions concentration of 250–1,000 mg L^{-1}. The pH was maintained at 3.0–4.5 for Pb(II) and Ni(II) ion solution at 25 °C. The solution was allowed to shake in a shaker at optimum conditions. On reaching the equilibrium time, the aqueous solutions were filtered using a 0.45 μm Whatman filter paper and analyzed with an AAS. The following formula was used to find the amount of metal ions adsorbed by the adsorbent at equilibrium:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{2}$$

where q_e is the adsorption capacity at equilibrium (mg g^{-1}), V is the volume of metal ion solution (g), C_e is the concentration of metal ions in the solution at equilibrium (mg L^{-1}), and m is the mass of adsorbent (g). The data obtained from the adsorption equilibrium studies were used to fit

with the different adsorption isotherm models to check the types of adsorption process. The two parameter models, namely, Langmuir (1918) and Freundlich (1906), and the three parameter models, namely, Redlich & Peterson (1959) and Sips (1948) were used to fit the adsorption equilibrium data.

Two parameter adsorption isotherm model

The Langmuir adsorption isotherm model of non-linear form is given as (Langmuir 1918):

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

where q_e is the adsorption capacity at equilibrium (mg g^{-1}), K_L is the Langmuir equilibrium constant related to the affinity of metal ions to the biosorbent (L mg^{-1}), q_m is the maximum monolayer adsorption capacity (mg g^{-1}), and C_e is the concentration of the metal ions in the solution at equilibrium (mg L^{-1}).

The Freundlich adsorption isotherm model is given as (Freundlich 1906):

$$q_e = K_F C_e^{1/n} \tag{4}$$

where K_F is the Freundlich constant [(mg g^{-1}) (L mg^{-1})$^{(1/n)}$] related to the bonding energy and n is a measure of the deviation from the linearity of adsorption (g/L). The significance of 'n' is as follows: $n = 1$ (linear); $n < 1$ (chemical process); $n > 1$ (physical process).

Three parameter adsorption isotherm model

The Redlich–Peterson adsorption isotherm model, a combination of Langmuir–Freundlich, is given as (Redlich & Peterson 1959):

$$q_e = \left(\frac{K_{RP} C_e}{1 + \alpha_{RP} C_e^{\beta_{RP}}} \right) \tag{5}$$

where K_{RP} is the Redlich–Peterson isotherm constant (L g^{-1}), β_{RP} is the exponent which lies between 0 and 1, α_{RP} is the Redlich–Peterson isotherm constant (L mg^{-1})$^{1/\beta_{RP}}$.

The significance of 'β' is as follows: $\beta = 1$ (Langmuir model); $\beta = 0$ (Freundlich model).

The Sips adsorption isotherm equation is given as (Sips 1948):

$$q_e = \left(\frac{K_S C_e^{\beta_s}}{1 + \alpha_S C_e^{1/\beta_s}} \right) \tag{6}$$

where α_s is the Sips model constant (L g^{-1})$^{1/\beta s}$, K_s is the Sips model isotherm constant (L g^{-1})$^{\beta s}$, and β_S is the Sips model exponent. The constant β_S is often regarded as the heterogeneity factor, with values close to 1 indicating a homogeneous binding site and values greater than 1 indicating a heterogeneous adsorption system.

Adsorption kinetic experiments

The adsorption kinetic studies were carried out by varying the contact time for the present adsorption system. The contact time was varied from 5 to 70 min and the temperature was maintained at a constant temperature of 25 °C. The metal ion concentration was varied from 250 to 1,000 mg L^{-1} while other parameters such as pH and adsorbent dosage were kept constant. The optimum pH for the Pb(II) and Ni(II) ions solution was fixed as 4.5. The known concentration of metal ion solutions along with the weighed adsorbent were placed in an Erlenmeyer flask. The adsorption mixtures were kept in a rotary shaking incubator. The samples were taken at various time intervals and then filtered using a 0.45 μm Whatman filter paper to get the supernatants. The collected supernatants were analyzed by using an AAS. The amount of Pb(II) and Ni(II) ions absorbed by the adsorbent at various time intervals is given by the following equation:

$$q_t = \frac{(C_o - C_t) V}{m} \tag{7}$$

where q_t is the quantity of metal ions absorbed onto the adsorbent at any time interval t (mg g^{-1}), C_o is the initial concentration of metal ions (mg L^{-1}), C_t is the concentration of metal ion solution at any time t (mg L^{-1}), m is the mass of the adsorbent (g), and V is the volume of the metal ion solution (L). The kinetics models such as pseudo-first order, pseudo-second order, and Elovich kinetic models were fitted with the observed kinetic data.

The pseudo-first order kinetic model is given by the following equation (Lagergren 1898):

$$q_t = q_e(1 - \exp(-k_1 t)) \tag{8}$$

where q_t is the quantity of metal ions adsorbed at any time t (mg g^{-1}), q_e is the quantity of metal ions adsorbed at equilibrium (mg g^{-1}), t is the time (min), and k_1 is the pseudo-first order kinetic rate constant (min^{-1}).

The pseudo-second order kinetic model is given by the following equation (Ho & McKay 1999):

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{9}$$

where q_t is the quantity of metal ions adsorbed at any time t (mg g^{-1}), q_e is the quantity of metal ions adsorbed at equilibrium (mg g^{-1}), t is the time (min), and k_2 is the pseudo-second order kinetic rate constant (g mg^{-1} min^{-1}).

The Elovich kinetic model is given by the following equation (Low 1960):

$$q_t = (1 + \beta_E) \, ln(1 + \alpha_E \beta_E t) \tag{10}$$

where α_E is the initial adsorption rate (mg g^{-1} min^{-1}), β_E is the desorption constant related to the activation energy of chemisorption (g mg^{-1}).

Adsorption thermodynamic study

In this thermodynamics study the adsorption process was carried out at different temperatures for a constant metal ion concentration of 100 mg L^{-1} and the adsorbent dosage was added as 1 g L^{-1}. After the adsorption process, the supernatant solution was analyzed using AAS and the observed results were used to find the thermodynamic parameters:

$$K_c = \frac{C_{Ae}}{C_e} \tag{11}$$

$$\Delta G^o = -RT \, \ln K_c \tag{12}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{13}$$

$$Log\, K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \tag{14}$$

where K_c is the equilibrium constant, C_{Ae} is the amount of metal ions adsorbed on the adsorbent per liter of solution (mg L^{-1}), C_e is the equilibrium metal ion concentration in solution (mg L^{-1}), T is the temperature (K), and R is the gas constant (8.314 J mol^{-1}K^{-1}).

RESULTS AND DISCUSSION

Effect of temperature and thermodynamic study

The effect of temperature on the adsorption of Pb(II) and Ni(II) ions using the microalga RH was examined at different temperatures (25 to 40 °C) with a fixed initial metal concentration (1,000 mg L^{-1}) at the adsorbent dose of 1 g L^{-1} and at a pH of 4.5. As Figure 1(a) and 1(b) illustrate, the percentage
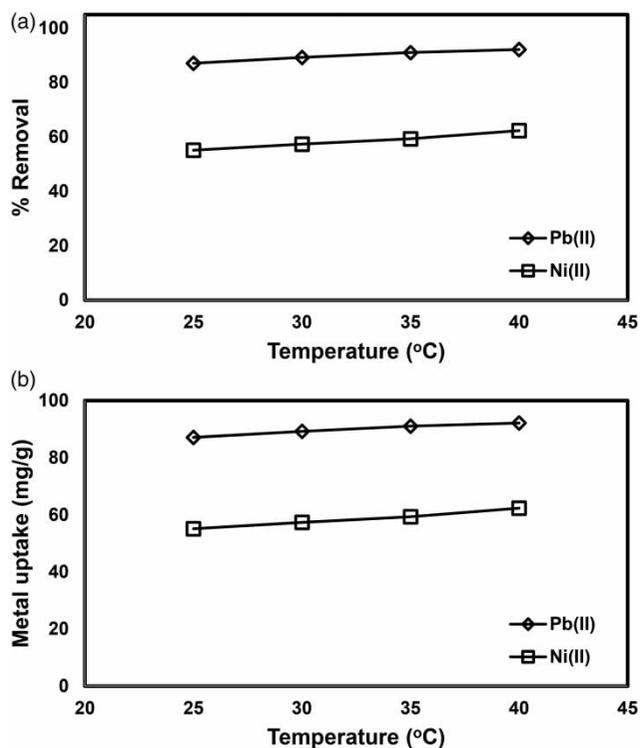

removal and metal uptake capacity of Pb(II) and Ni(II) ions onto the adsorbent was slightly dependent on the solution temperature. It can be seen that the sorption of Pb(II) and Ni(II) ions increased gradually with the increase in the temperature. This might be due to more availability of active sites on the surface of the RH or the decrease of the layer thickness that surrounds the adsorbent. The results suggest that the adsorption process of Pb(II) and Ni(II) ions is endothermic in nature which means that the adsorption capacity was directly proportional to the solution temperature.

The results obtained from the temperature studies were used to estimate thermodynamic parameters such as Gibbs free energy (ΔG^o, kJ mol^{-1}), entropy (ΔS^o, kJ mol^{-1}), and enthalpy (ΔH^o, kJ mol^{-1}). Gibbs free energy (ΔG^o) was calculated from Equations (11) and (12). The values of ΔH^o and ΔS^o were calculated from the slope and the intercept of the linear plot of *log K_c* versus *1/T* (Figure 2). The estimated thermodynamic parameters for the adsorption of Pb(II) and Ni(II) ions using RH are shown in Table 1. The negative value of Gibbs free energy increased when the temperature was increased from 25 to 30 °C, which suggests that a greater number of active sites was available at higher temperature, and it was concluded that the adsorption process was a spontaneous process. The positive value of standard enthalpy change (ΔH^o) and the standard entropy change (ΔS^o) indicated that the adsorption process was an endothermic process and enthalpy driven, respectively.

Effect of particle size

The particle size of RH was an influence in the removal of Pb(II) and Ni(II) ions from the aqueous solution. The
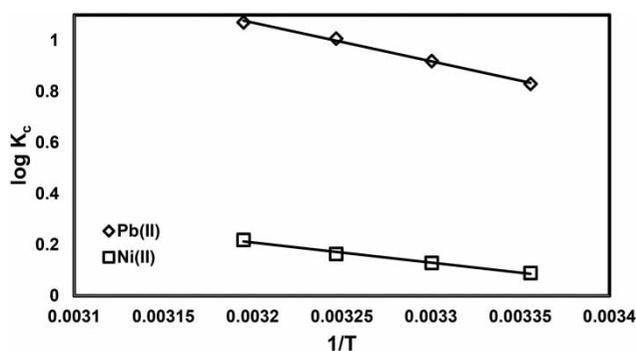

Figure 1 | (a) Effect of temperature on the removal of metal ions by RH. (b) Effect of temperature on metal uptake by RH.

Figure 2 | Thermodynamic study on the removal of metal ions by RH.

Table 1 │ Thermodynamic parameters for the adsorption of metal ions onto RH

Metal ions	ΔH^o (kJ/mol)	ΔS^o (J/mol/K)	ΔG^o (kJ/mol)			
			25 °C	30 °C	35 °C	40 °C
Pb(II)	28.950	113.14	−4.736	−5.332	−5.940	−6.416
Ni(II)	15.103	52.329	−0.511	−0.749	−0.968	−1.312

effect of particle size on the removal and metal uptake capacity of Pb(II) and Ni(II) ions using the RH was examined and the results are shown in Figure 3(a) and 3(b). Four different particle sizes, 0.5, 0.6, 0.7, and 1.0 mm were tested to find the optimum size for the maximum removal of Pb(II) and Ni(II) ions from the aqueous solution. The results from Figure 3(a) and 3(b) clearly show the considerable deviations in the percentage removal and metal uptake capacity of Pb(II) and Ni(II) ions using the different particle sizes of adsorbent material. Consequently, the smallest particle size of 0.5

mm has better removal efficiency and metal uptake capacity when compared with 0.6, 0.7, and 1.0 particle sizes. Generally, the larger particle size has a tortuous pathway, longer diffusion path length to its interior surface and diffusional resistance due to the restriction posed by the pore size. Conversely, the particle size of 0.5 mm adsorbent material has a larger surface area which enhances the adsorption capacity. Therefore, the particle size of 0.5 mm was selected as the optimum particle size for the effective removal of Pb(II) and Ni(II) ions.
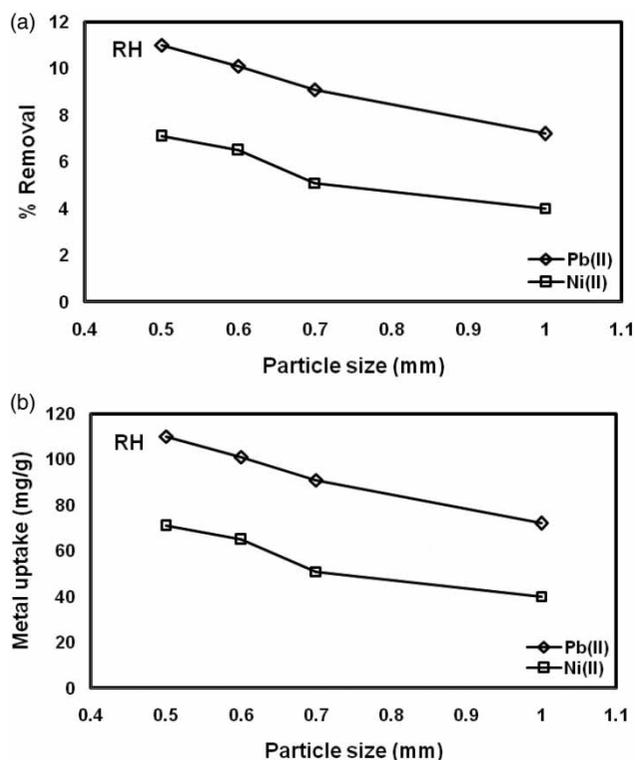

Figure 3 │ (a) Effect of particle size on the biosorption of metal ions by RH (initial metal ion concentration = 1,000 mg/L, biosorbent dose = 1 g/L, pH = 4.5, time = 60 min, and temperature = 25 °C). (b) Effect of particle size on the metal uptake by RH (initial metal ion concentration = 1,000 mg/L, biosorbent dose = 1 g/L, pH = 4.5, time = 60 min, and temperature = 25 °C).
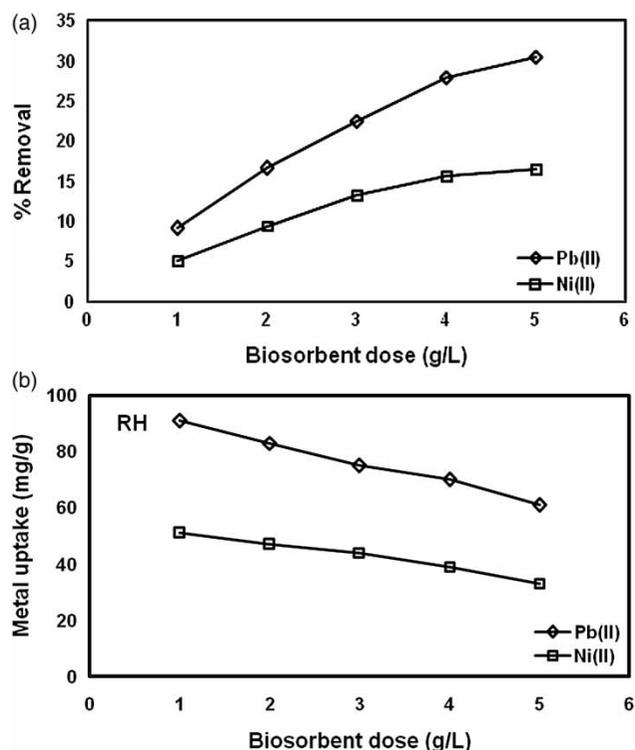

Figure 4 │ (a) Effect of adsorbent dose on the removal of metal ions by RH (initial metal ion concentration = 1,000 mg/L, particle size = 0.7 mm, pH = 4.5, time = 60 min, and temperature = 25 °C). (b) Effect of adsorbent dose on the metal uptake by RH (initial metal ion concentration = 1,000 mg/L, particle size = 0.7 mm, pH = 4.5, time = 60 min, and temperature = 25 °C).

Effect of adsorbent dose

Adsorbent dosage is an important operating parameter to maximize the interaction between the metal ions in the liquid phase and the active sites of adsorbent in the solid phase. The effect of RH dosage on the removal and metal uptake capacity of Pb(II) and Ni(II) ions is shown in Figure 4(a) and 4(b). The results from Figure 4(a) clearly show that the removal of metal ions was increased with an increase in adsorbent dose from 1.0 to 5.0 g L^{-1}. This may be due to the fact that the active sites of the adsorbent were increased with the increase in the adsorbent dose. The equilibrium adsorption capacity value was decreased with the increase in adsorbent dose. This result might be due to the availability of more active sites at lower dosage as compared to higher dosage, which has less active sites
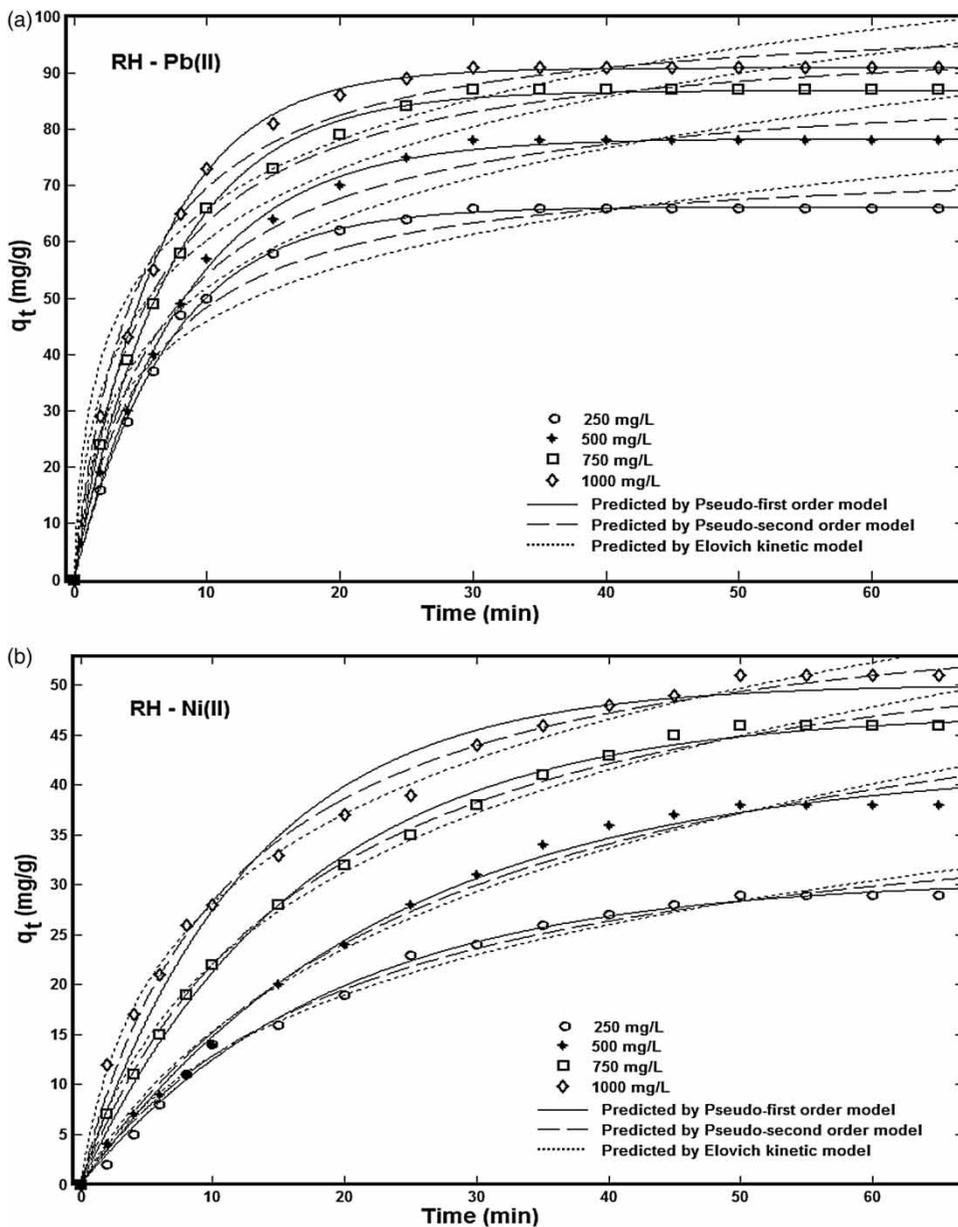

Figure 5 │ (a) Adsorption kinetic model for removal of Pb(II) ions by RH. (b) Adsorption kinetic model for removal of Ni(II) ions by RH.

to adsorb the metal ions in the solution because of the aggregation or overlying of metal ions on the active sites that decrease the effective surface area for the adsorption process. Moreover, this result might be attributed to the insufficiency of Pb(II) and Ni(II) ions in the adsorbate solution with respect to available active sites or the existence of interference between the active sites and adsorbent material. For the present adsorption system, 1 g/L was sufficient for the removal of metal ions from the wastewater.

Table 2 | Kinetic parameters for the adsorption of Pb(II) ions onto RH

Kinetic model	Parameters	Concentration of Pb(II) ion solution (mg/L)			
		250	500	750	1,000
Pseudo-first order equation	k_1 (min^{-1})	0.1418	0.1225	0.1397	0.1602
	q_e, cal (mg/g)	74.88	90.03	98.16	101.2
	R^2	0.9847	0.9883	0.9919	0.9896
	SSE	102	112.4	89.8	120.6
	RMSE	2.608	2.738	2.447	2.835
Pseudo-second order equation	k_2 (g/mg.min)	0.002441	0.00168	0.001859	0.002173
	q_e, cal (mg/g)	66.18	78.33	86.84	90.86
	q_e, exp (mg/g)	66.53	78.21	87.15	91.36
	R^2	0.999	0.9982	0.9972	0.9979
	SSE	6.837	17.1	31.75	23.92
	RMSE	0.6751	1.068	1.455	1.263
Elovich kinetic equation	α (mg/g.min)	0.4385	0.2208	0.3334	0.563
	β (g/mg)	5.263	7.025	7.15	6.793
	R^2	0.9433	0.9567	0.9596	0.9506
	SSE	378.5	417.6	450.4	575.1
	RMSE	5.023	5.276	5.48	6.192

Table 3 | Kinetic parameters for the adsorption of Ni(II) ions onto RH

Kinetic model	Parameters	Concentration of Ni(II) ion solution (mg/L)			
		250	500	750	1,000
Pseudo-first order equation	k_1 (min^{-1})	0.05265	0.04359	0.05994	0.0795
	q_e, cal (mg/g)	40.58	58.14	60.51	60.63
	R^2	0.9923	0.9914	0.9963	0.9789
	SSE	13.07	26.2	14.18	84.88
	RMSE	0.9334	1.322	0.9722	2.379
Pseudo-second order equation	k_2 (g/mg.min)	0.001146	0.0006106	0.0009479	0.00145
	q_e, cal (mg/g)	30.6	42.03	47.24	52.13
	q_e, exp (mg/g)	29.18	38.23	46.62	51.74
	R^2	0.9959	0.9962	0.9975	0.9931
	SSE	7.041	11.4	9.571	27.8
	RMSE	0.6851	0.8718	0.7988	1.361
Elovich kinetic equation	α (mg/g.min)	0.04532	0.0185	0.04457	0.1128
	β (g/mg)	4.232	7.018	6.234	5.296
	R^2	0.9849	0.9851	0.9929	0.9953
	SSE	25.72	45.34	27.23	18.86
	RMSE	1.309	1.739	1.347	1.121

Adsorption kinetics

Adsorption kinetics is an important tool for the design of the adsorption system. The adsorption mechanism mainly depends on many factors such as structure of the adsorbent, physical and chemical characteristics of the solute and the adsorbent material which describes the reaction rates and reaction pathways. The adsorption rate constant and the order of adsorption rate kinetics are the main physico-chemical parameters that are needed to estimate the basic

good qualities of the adsorbent. In this work, the pseudo-first order, pseudo-second order, and Elovich kinetic model have been used to fit the adsorption kinetic data at different initial Pb(II) and Ni(II) ion concentrations (250, 500, 750, and 1,000 mg L^{-1}). The kinetic parameters and other values were determined using the linear plots of time (min) vs qt (mg g^{-1}) and the results are shown in Figure 5(a) and 5(b). The calculated values of kinetic parameters and the other values of each kinetic model are shown in Tables 2 and 3 for Pb(II) and Ni(II) ions,
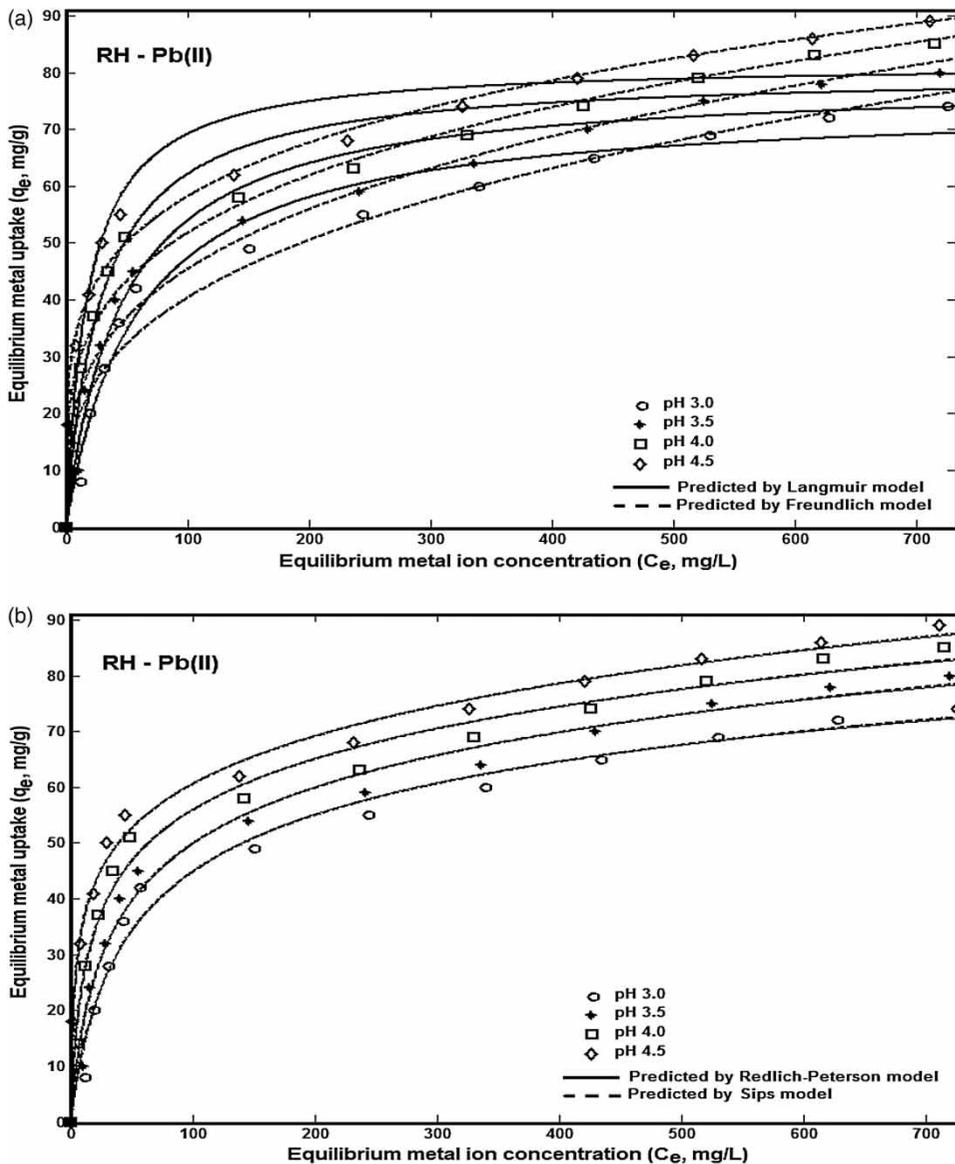

Figure 6 | (a) Adsorption isotherm (two parameter model) plots for removal of Pb(II) ions by RH. (b) Adsorption isotherm (three parameter model) plots for removal of Pb(II) ions by RH.
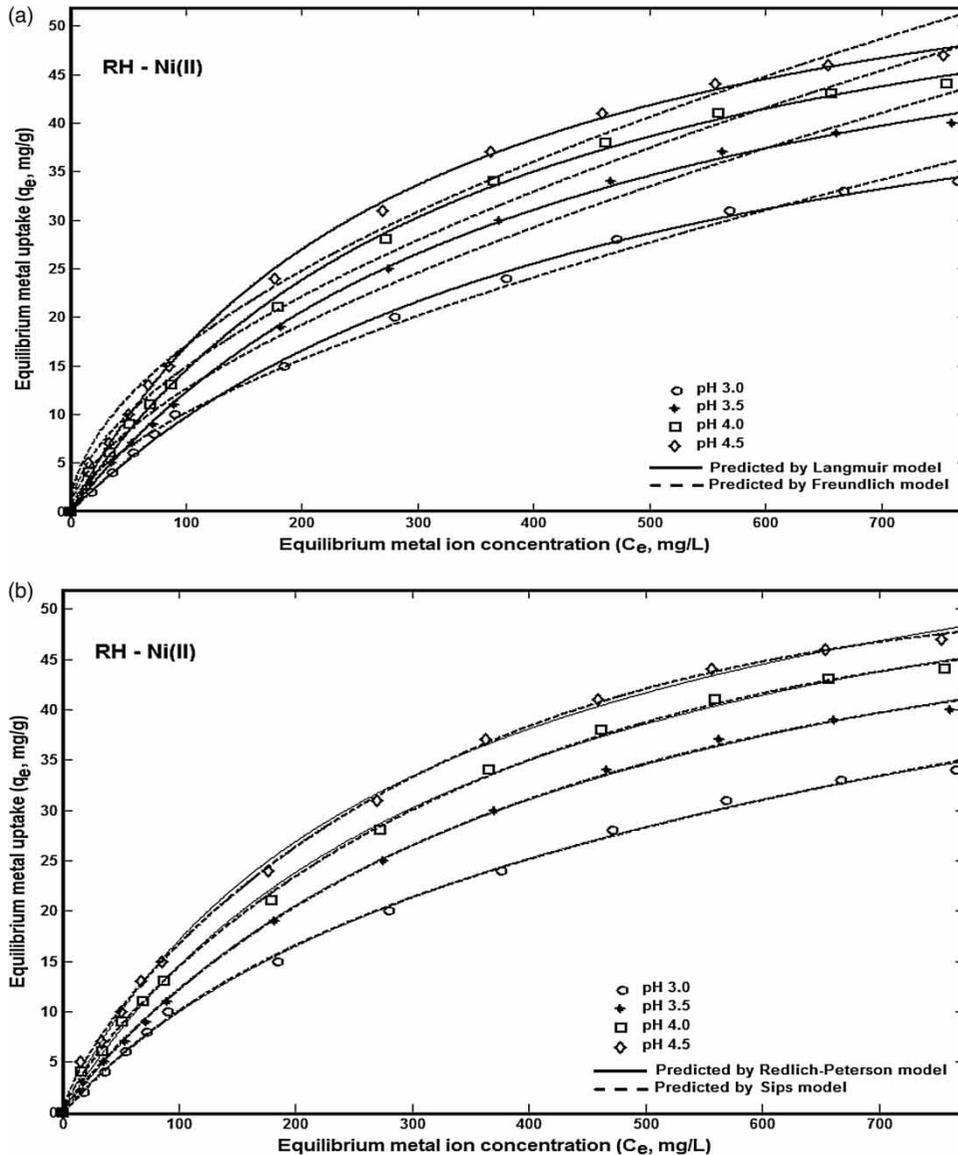
Figure 7 | (a) Adsorption isotherm (two parameter model) plots for removal of Ni(II) ions by RH. (b) Adsorption isotherm (three parameter model) plots for removal of Ni(II) ions by RH.

respectively. The determination of correlation coefficient values of pseudo-second order kinetics [0.999, 0.9982, 0.9972, and 0.9979 for Pb(II); 0.9959, 0.9962, 0.9975, and 0.9931 for Ni(II)] were higher than the other kinetic models, which indicated that the adsorption kinetic data follows the pseudo-second order kinetic model. Tables 2 and 3 show that the experimental values of adsorption capacity (q_e, exp) were very close to the theoretical adsorption capacity (q_e, cal) of the pseudo-second order kinetic model. The results suggest that the pseudo-second order

kinetics is more applicable for the adsorption of Pb(II) and Ni(II) ions onto the RH. Consequently, the chemical adsorption was accepted as the rate controlling step in the present adsorption system.

Adsorption isotherm

Adsorption isotherm plays a vital role in optimizing the design of an adsorption system. The adsorption isotherm study gives the specific relationship between the

concentration of adsorbate in the liquid solution and the concentration of metal ions on the adsorbent surface at equilibrium. The equilibrium adsorption isotherm of Pb(II) and Ni(II) ions onto the RH were determined at different pH (3.0, 3.5, 4.0, and 4.5) values. In this study, two parameter (Langmuir and Freundlich) and three parameter (Redlich–Peterson and Sips) isotherm models were used to evaluate the equilibrium isotherm data (C_e vs q_e) and the results are shown in Figures 6(a) and 6(b) and 7(a) and 7(b). The Langmuir constants (K_L and q_m), Freundlich isotherm constants (K_L and n), Redlich–Peterson isotherm constants (β_{RP}, K_{RP}, and α_{RP}), and Sips model constants (β_S, K_S, and α_S), along with correlation coefficient values (R^2) and the error values (SSE and $RMSE$) are summarized in Tables 4 and 5. The data obtained from Tables 4 and 5 show that the Sips isotherm model has higher correlation coefficient values [0.9848, 0.9861, 0.9889, and 0.995 for Pb(II) and 0.9983, 0.9995, 0.9992, and 0.9994 for Ni(II)] and low error values compared to the other isotherm models, which indicated that the adsorption process follows the Sips isotherm

model. The maximum monolayer adsorption capacity was found to be 81.7 mg g^{-1} and 65.81 mg g^{-1} for Pb(II) and Ni(II) ions, respectively, at optimum conditions. Based on the correlation coefficient values, the experimental data gave admirable fits within the following isotherm order: Sips > Redlich–Peterson > Langmuir > Freundlich for both Pb(II) and Ni(II) ions.

The maximum monolayer adsorption capacity (q_{max}) of the present adsorbent was compared with the other adsorbents for the removal of metal ions (Table 6). The results show that the RH was found to be higher for metal ions as compared to the other low-cost adsorbents.

CONCLUSION

Based on the observations in the present study, it can be concluded that the microalga RH is an effective adsorbent for the removal of Pb(II) and Ni(II) ions from aqueous solution due to high efficiency, low-cost, reusability, and fast

Table 4 │ Isotherm constants of two parameter and three parameters models for the removal of Pb(II) ions by the RH

Adsorption isotherm models	pH	3.0	3.5	4.0	4.5
Two-parameter model constants					
Langmuir	q_m (mg/g)	74.82	78.6	80.05	81.7
	K_L (L/mg)	0.01733	0.022	0.0348	0.05554
	R^2	0.9767	0.972	0.9648	0.9473
	SSE	169.9	229.4	306.5	482.9
	$RMSE$	3.93	4.567	5.279	6.626
Freundlich	K_F [(mg/g)(L/mg)$^{(1/n)}$)]	9.167	11.49	15.93	21.54
	n (g/L)	3.105	3.348	3.904	4.63
	R^2	0.9619	0.9677	0.9734	0.987
	SSE	277.6	265	231	119.5
	$RMSE$	5.024	4.909	4.583	3.295
Three-parameter model constants					
Redlich–Peterson	K_{RP} (L/g)	1.845	2.913	6.003	21.94
	a_{RP} (L/mg)$^{(1/\beta RP)}$	0.05625	0.09738	0.2012	0.7795
	β_{RP}	0.8715	0.8481	0.8421	0.8271
	R^2	0.9837	0.985	0.988	0.9948
	SSE	118.6	122.7	104.2	47.92
	$RMSE$	3.444	3.503	3.228	2.189
Sips	K_S (L/g)$^{\beta s}$	1.567	2.445	5.174	20.65
	a_s (L/mg)$^{(\beta s)}$	0.05554	0.09132	0.1851	0.7572
	β_S	1.077	1.087	1.087	1.093
	R^2	0.9848	0.9861	0.9889	0.995
	SSE	110.8	114.1	96.33	46.19
	$RMSE$	3.328	3.378	3.104	2.149

Table 5 | Isotherm constants of two parameter and three parameter models for the removal of Ni(II) ions by the RH

Adsorption isotherm models	pH	3.0	3.5	4.0	4.5
Two-parameter model constants					
Langmuir	q_m (mg/g)	55.48	63.14	65.66	65.81
	K_L (L/mg)	0.00213	0.00242	0.00285	0.00348
	R^2	0.9979	0.9992	0.9982	0.9982
	SSE	3.819	1.994	5.552	6.298
	RMSE	0.5892	0.4258	0.7104	0.7567
Freundlich	K_F ((mg/g)(L/mg)$^{(1/n)}$))	0.5753	0.7775	1.065	1.436
	n (g/L)	1.604	1.652	1.746	1.859
	R^2	0.9927	0.9878	0.9883	0.9877
	SSE	13.59	32.47	36.84	43.42
	RMSE	1.111	1.718	1.83	1.987
Three-parameter model constants					
Redlich–Peterson	K_{RP} (L/g)	0.1353	0.1527	0.1884	0.2428
	a_{RP} (L/mg)$^{(1/\beta RP)}$	0.00741	0.00242	0.00301	0.00539
	β_{RP}	0.8417	0.8459	0.9934	0.9447
	R^2	0.9982	0.9992	0.9982	0.9983
	SSE	3.312	1.994	5.549	5.976
	RMSE	0.5755	0.4258	0.7449	0.773
Sips	K_S (L/g)$^{\beta s}$	0.08437	0.2136	0.3878	0.5677
	a_s (L/mg)$^{(\beta s)}$	0.01629	0.000707	0.00018	0.00009
	β_S	1.17	0.9031	0.7986	0.7444
	R^2	0.9983	0.9995	0.9992	0.9994
	SSE	3.116	1.45	2.675	1.963
	RMSE	0.5582	0.3808	0.5172	0.4431

Table 6 | Comparison of maximum monolayer adsorption capacity of the RH with different adsorbents

Heavy metal ions	Adsorbents	q_m (mg/g)	References
Pb(II)	Sugarcane bagasse	6.37	Martin-Lara *et al.* (2010)
Pb(II)	Sugarcane bagasse treated by H_2SO_4	7.30	Martin-Lara *et al.* (2010)
Pb(II)	Heartwood of *Areca catechu* powder	11.723	Chakravarty *et al.* (2010)
Pb(II)	Cashew nut shell	17.82	Kumar (2014)
Pb(II)	Chitosan–polyacrylonitrile blend	20.08	Anitha *et al.* (2015)
Pb(II)	Saw dust	21.05	Li *et al.* (2007)
Pb(II)	Hazelnut shell	28.18	Pehlivan *et al.* (2009)
Pb(II)	***Rhizoclonium hookeri***	**81.70**	**This study**
Ni(II)	*Chlorella vulgaris*	0.6	Wong *et al.* (2000)
Ni(II)	*Chlorella miniata*	1.4	Wong *et al.* (2000)
Ni(II)	Tea industry waste	5.0	Ahluwalia & Goyal (2005)
Ni(II)	Modified coir pith	38.9	Ewecharoen *et al.* (2008)
Ni(II)	Mango peel	39.75	Iqbal *et al.* (2009)
Ni(II)	*Polyporous versicolor*	57	Dilek *et al.* (2002)
Ni(II)	***Rhizoclonium hookeri***	**65.81**	**This study**

kinetics. In batch adsorption experiments, the removal of Pb(II) and Ni(II) ions were influenced by the different operating parameters, such as solution pH, adsorbent dose, particle size, initial metal ion concentration, time, and temperature. The experimental data have been analyzed by several adsorption isotherm (Langmuir, Freundlich, Redlich–Peterson, and Sips models) and kinetic models (pseudo-first order, pseudo-second order, and Elovich kinetic models). The Sips isotherm and pseudo-second order kinetic model were more applicable for the adsorption of Pb(II) and Ni(II) ions onto the RH as shown from the statistical parameters. The maximum monolayer adsorption capacity was found to be 81.7 mg g^{-1} and 65.81 mg g^{-1} for Pb(II) and Ni(II) ions, respectively. The thermodynamic studies showed that the adsorption process was spontaneous, enthalpy driven, and endothermic in nature.

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