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Biosorption and Desorption of Lead(II) by *Hydrilla verticillata*

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ABSTRACT The potential of nonliving biomass of *Hydrilla verticillata* to adsorb Pb(II) from an aqueous solution containing very low concentrations of Pb(II) was determined in this study. Effects of shaking time, contact time, biosorbent dosage, pH of the medium, and initial Pb(II) concentration on metal-biosorbent interactions were studied through batch adsorption experiments. Maximum Pb(II) removal was obtained after 2 h of shaking. Adsorption capacity at the equilibrium increased with increasing initial Pb(II) concentration, whereas it decreased with increasing biosorbent dosage. The optimum pH of the biosorption was 4.0. Surface titrations showed that the surface of the biosorbent was positively charged at low pH and negatively charged at pH higher than 3.6. Fourier transform infrared (FT-IR) spectra of the biosorbent confirmed the involvement of hydroxyl and C=O of acylamide functional groups on the biosorbent surface in the Pb(II) binding process. Kinetic and equilibrium data showed that the adsorption process followed the pseudo-second-order kinetic model and both Langmuir and Freundlich isothermal models. The mean adsorption energy showed that the adsorption of Pb(II) was physical in nature. The monolayer adsorption capacity of Pb(II) was 125 mg g^{-1}. The desorption of Pb(II) from the biosorbent by selected desorbing solutions were $HNO_3 > Na_2CO_3 > NaOH > NaNO_3$.

KEYWORDS biosorption, desorption, *Hydrilla verticillata*, isothermal models, kinetics, Pb(II), surface titration

INTRODUCTION

Heavy metal pollution is a major environmental threat all over the world. In developing countries, where enforcement of environmental regulations is less stringent, heavy metals enter the food chain through agricultural produce. Bioaccumulation of heavy metals causes serious ecological and health hazards (Zhang et al. 2013). Industrial effluents are one of the major sources of heavy metal contamination in water resources on earth.

Pb(II) is commonly found in wastewater discharged from industries manufacturing batteries, paints, cables, metal alloys, and plastics (Sari and Tuzen 2008). Pb(II) is absorbed into the human body from contaminated environments, by inhaling, orally, or through the skin. In oral toxification, the

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gastrointestinal tract absorbs 5–15% of lead, which is mainly retained in the bones (Athar and Vohora 1995). According to a report from the United States Environmental Protection Agency (US EPA), a lead level of 10 μg/dl in blood causes lead poisoning in young children (US EPA 2013).

Heavy metals are toxic even at low concentrations (Zhang et al. 2013). Therefore, pretreatment of effluents containing heavy metals before their discharge into the environment is necessary to reduce environmental pollution and safeguard the health of humans. Several conventional physicochemical methods, such as membrane filtration (Molinari, Argurio, and Poerio 2004), chemical precipitation (Ramos et al. 2009), ion exchange (Inglezakis and Loizidou 2007), chemical oxidation or reduction (Mitra et al. 2011), electrochemical treatment (Rana, Mohan, and Rajagopal 2004), solvent extraction (Miretzky, Saralegui, and Cirelli 2006), and activated carbon adsorption (Malik 2003), have been used to remove heavy metals and other contaminants from effluents. As many of these methods are expensive and inefficient at low metal concentrations, there is a necessity for cost-effective, alternative technologies for the treatment of metal-contaminated aqueous and nonaqueous systems.

The biosorption process utilizes the ability of nonliving biological materials to accumulate heavy metals from waste streams by either metabolically mediated or purely physicochemical pathways of uptake (Fourest and Roux 1992; Mohanty et al. 2006). Since biosorption is a low-cost, environmental friendly technique, it can be easily adopted by developing countries. This biosorption technology can be applied in large-scale applications such as treatment of industrial effluent using fixed-bed column reactors. In this process, the metal-contaminated wastewater is allowed to flow through the column filled with the biosorbent at a controlled rate. Metal ions in the wastewater are then adsorbed on to the biosorbent, as it passes through the column, and the metal free wastewater is discharged into the environment. Biosorption of Pb(II) from aqueous solutions has been investigated by using various biosorbents, such as microbial biomass (Cabuk et al. 2007; Saiano et al. 2005; Zhang et al. 2013), waste tea leaves (Ahluwalia and Goyal 2005), fish scales (Basu et al. 2007), algae (Lodeiro et al. 2006; Sari and Tuzen 2008), rice husk (Tarley et al. 2004), and seed shells of star apples (Onwu and Ogah 2010).

Hydrilla verticillata is a perennial submerged fresh water aquatic plant commonly found in many parts of the world. In most countries, including Sri Lanka, it grows as a weed in freshwater bodies. In this study, nonliving biomass of *H. verticillata* was used as a biosorbent to remove Pb(II) from aqueous solution. Preliminary experiments of Huang et al. (2009) has shown the Pb(II) biosorption performance of *H. verticillata* in a solution containing 100 mg L^{-1} of Pb(II). The objective of this study was to investigate the potential of nonliving *H. verticillata* to adsorb Pb(II) from a solution containing very low Pb(II) concentration (i.e., 5.00 mg L^{-1}). Further, the surface of the biosorbent was characterized through surface titration and Fourier transform infrared (FT-IR) analysis. Several parameters that affect the extent of the biosorption, such as shaking time, shaking speed, and pH of the medium, were optimized through batch adsorption experiments. Equilibrium data and kinetics of the adsorption process were also studied. A batch desorption study was carried out to select a suitable desorbing agent to recover Pb(II) from the biosorbent.

MATERIALS AND METHODS

Sampling of Biosorbent

Fresh *H. verticillata* was collected randomly from a water stream in Colombo, Sri Lanka, and washed thoroughly with tap water, followed by deionized water. The identification of the plant species was confirmed by comparing with an authenticated sample in the *National Herbarium*. The biomass was air dried for 2 days and oven dried at 70°C for 3 days (higher temperatures were not used to avoid possible decomposition of organic matter). The dried biomass (biosorbent) was ground and sieved to obtain the fraction of diameter between 297 and 350 μm to be used in all experiments, conducted in triplicate whenever necessary.

Surface Characteristics of Adsorbent

Nitrogen gas was bubbled through a suspension of 1.0 g of biosorbent in 100 ml of $NaNO_3$ solution of known concentration while stirring at a constant rate for 3 h to remove dissolved CO_2. The vessel containing the suspension was sealed, and stirring was continued for 12 h in a CO_2-free environment to obtain a homogeneous solution. The initial pH of the

suspension was measured using a pH meter (Thermo Russell model RL060P; Singapore) and a NaOH solution of known concentration was added to reach pH 10.0. The mixture was then titrated by adding small aliquots of HNO_3 of known concentration, and the pH was measured after each addition. The system was allowed to have an adequate equilibration time after each addition before recording the pH measurement. The titration was continued until the pH of the system reached a value of 3.0. The system was continuously and steadily stirred and purged with N_2 throughout the titration. A back titration was carried out using the same NaOH solution, whereas a blank titration was conducted in the absence of the biosorbent. The entire procedure was repeated for two more ionic strengths.

Determination of Surface Area

The specific surface area of the biosorbent particles was determined by the methylene blue adsorption method (Hang and Brindley 1970). A series of methylene blue solutions of different concentrations ranging from 1.0×10^{-6} to 5.0×10^{-6} mol L^{-1} was prepared. Biosorbent suspensions were then prepared by mixing 5 mg of the biosorbent in 100 ml each of methylene blue solution and stirred gently for 3 h to ensure that adsorption equilibrium was reached. Suspensions were centrifuged and the supernatants were analyzed for remaining methylene blue concentration by UV-visible spectrophotometry (Shimadzu model UV-160 A; Koyoto, Japan) at the wavelength of 665 nm.

Effect of Shaking Speed

Batch adsorption studies were carried out by mixing 0.200 g of biosorbent in 100.00 ml of metal ion solution and shaking the suspensions at different shaking speeds. Lead(II) nitrate (Aldrich, Steinheim, Germany) was dissolved in deionized water to prepare Pb(II) stock solutions. The initial metal ion concentration was 5.00 mg L^{-1}, and the initial pH of the system was maintained at 5.00. Suspensions were shaken on an orbital shaker for 30 min and filtered. Subsequently, the filtrates were analyzed for remaining Pb(II) concentration by atomic absorption spectrophotometry (AAS) (model GBC 933AA; Melbourne, Australia) at the wavelength of 217.0 nm using air-acetylene flame.

Effect of Contact Time and Settling Time

Three different dosages of the *H. verticillata* biosorbent (i.e., 1.0, 2.0, 4.0 g/L) were introduced individually into 100.00 ml of 5.00 mg L^{-1} of metal ion solutions at pH 5.00 and at 25°C in Erlenmeyer flasks, and the suspensions were shaken on an orbital shaker at 140 rpm to allow interaction between the two phases. The initial pH of the metal ion solution was adjusted to the desired value by adding HNO_3 or NaOH. The suspensions were removed from the shaker at predetermined time intervals and filtered. Filtrates were analyzed for residual Pb(II) concentrations by AAS to determine the optimum shaking time.

To determine the optimum settling period, 0.200 g of the biosorbent was shaken in 100.00 ml of metal ion solution under similar conditions, keeping the optimum shaking time and allowing to settle for different time intervals. The optimum settling time was then determined. The native biomass was digested in nitric acid using a microwave digester (Milestone model START D; Sorisole, Italy), to determine the presence of lead on it before the adsorption process. Fourier transform infrared (FT-IR) spectra of the biosorbent before and after adsorption of Pb(II) were recorded using a FT-IR spectrophotometer (Nicolet model 6700; Madison, WI). The sample disks used for FT-IR analysis were prepared in anhydrous KBr and the spectral range varied from 4000 to 400 cm^{-1}.

Effect of Initial pH and Pb(II) Concentration of the Medium

To study the effect of pH on the biosorption processes, 200 mg of the biosorbent was thoroughly mixed individually with 100.00 ml of Pb(II) ion solutions at ambient temperature, each of which was prepared at a different pH between 2.0 and 10.0 using HNO_3 and NaOH solutions. The initial concentration of Pb(II) in solutions at pH 5.0 was varied from 2.00 to 50.00 mg L^{-1} to determine the effect of initial metal ion concentration on the biosorption. The suspensions were shaken, allowed to settle, and the filtrates were analyzed by AAS to determine the concentration of Pb(II) remaining in the suspensions.

Desorption of Pb(II) from Metal-Loaded Biomass

Pb(II) was loaded on to the *H. verticillata* biomass by mixing 0.200 g of the biosorbent in 100.00 ml of 5.00 mg L^{-1} Pb(II) solution at pH 5.0. Suspensions were shaken at 140 rpm for 2 h to achieve the maximum adsorption of Pb(II) on to the biomass. Subsequently, metal-loaded biomass was separated from the suspensions by filtering, washed gently with distilled water, and dried at 60°C for 24 h. Desorption process was studied to determine the best desorbing solution to recover Pb(II) from the metal-loaded biosorbent after a biosorption process. Batch experiments were carried out by shaking 0.100 g of dried metal-loaded biomass in 100.00 ml of various desorbing solutions, including HNO_3, NaOH, Na_2CO_3, and $NaNO_3$, for 1 h on an orbital shaker at 140 rpm shaking speed. Suspensions were filtered, and the filtrates were analyzed by AAS to determine the amount of Pb desorbed into the desorbing solution.

RESULTS AND DISCUSSION

Surface Characteristics of Adsorbent

The surface charge density (σ) at each pH was calculated using Equation 1 (Priyantha et al. 2009).

$$\sigma = \{[F/(a \times s)]\}\{(C_a - C_b) - [H^+] + [OH^-]\} \quad (1)$$

where F is the Faraday constant, a is the mass of the biosorbent in the suspension (1.0 g), C_a and C_b are the calculated concentrations of the acid and the base, respectively, in the medium at a particular point of titration, and $[H^+]$ and $[OH^-]$ are the hydrogen and hydroxyl ion concentrations in the medium according to the measured pH value at a particular point of titration. The specific surface area (s) was estimated to be 2.9 $m^2\ g^{-1}$ using Equation 2,

$$s = M_{mb} \times 6.02 \times 10^{23} \times A_{mb}/m \quad (2)$$

where M_{mb} is the number of moles of methylene blue adsorbed for the completion of a monolayer, and it was obtained as 1.8×10^{-8} moles from the methylene blue test. A_{mb} is the surface area per methylene blue molecule (130 $Å^2$), and m is the amount of the biosorbent in the suspension (5 mg).

The surface charge of the biosorbent was determined to be highly dependent on the pH of the medium (Figure 1). Since the number of protons bound to the surface of the biosorbent is calculated to obtain the ultimate result of surface charge density, it is assumed that no ion other than protons in the medium binds to the biosorbent during surface titrations (Butt, Graf, and Kappl 2003). The importance of using $NaNO_3$ in surface titrations is that its constituent ions do not bind specifically to the biosorbent surface.

As depicted in Figure 1, surface charge density decreased with increasing pH, and the biosorbent surface was negatively charged at pH > 3.6 for ionic strengths between 0.001 and 0.1 M, which includes typical concentrations of ions in wastewater. Moreover, the surface charge density versus pH curves plotted for different ionic strengths intersect at a common point of pH = 6.5. Further, the biosorbent surface becomes either more positive or negative at a particular pH when the ionic strength is increased from 0.001 to 0.1 M. Increase in surface charge with increasing ionic strength is due to the increase in the capacitance of the electric double layer, resulting in increased charge for a given surface potential (Butt, Graf, and Kappl 2003).

Effect of Shaking Speed

The biosorption of Pb(II) by dry biomass of *H. verticillata* increased with increasing shaking speed and reached a maximum at 180 rpm speed, and thereafter the adsorption was reduced by further increase of the

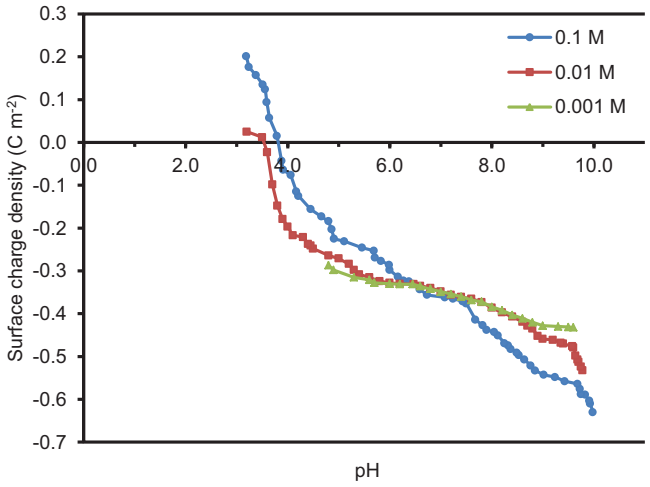

FIGURE 1 Variation of surface charge density of *H. verticillata* biomass with solution pH in $NaNO_3$ solutions of different ionic strengths.

shaking speed (Figure 2). The percentage removal was determined using Equation 3, where C_i and C_f are the initial and the final concentrations of Pb(II) in the system, respectively.

$$\text{Percentage removal} = [(C_i - C_f)/C_i] \times 100 \quad (3)$$

Shaking induces collisions between the metal ions and the biosorbent particles. These collisions are necessary for a successful biosorption process. When the shaking speed is increased, frequency of the collisions increases so that the removal percentage increases. However, increase in the agitation speeds increases the mobility of the two phases (i.e., metal ion and biosorbent), which does not provide adequate time for the metal to be adsorbed on to the biosorbent surface. Moreover, higher speeds may also result in the detachment of already adsorbed metal ions. Therefore, the removal capacity drops at extremely high shaking speeds. However, despite 180 rpm being the optimum shaking speed, 140 rpm, which was the next best speed, was used as the default shaking speed in all other experiments to overcome the practical inconveniences.

Effect of Contact Time and Settling Time

Analysis of digested samples of original *H. verticillata* confirms the absence of lead in the biosorbent before the adsorption process. The percentage removal of Pb (II) by *H. verticillata* is shown as a function of shaking time in Figure 3. A rapid removal of Pb(II) from the aqueous solution was recorded during the first 20 min

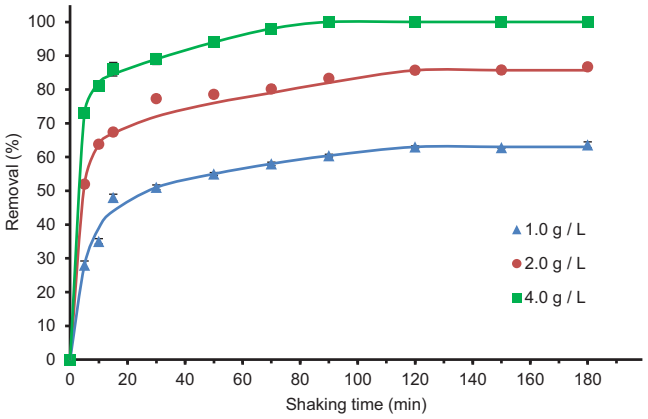

FIGURE 3 Percentage removal of Pb(II) by dry *H. verticillata* biosorbent at different shaking times for different biosorbent concentrations (initial Pb(II) ion concentration = 5.00 mg L^{-1}, pH = 5.0, temperature = 25°C, shaking speed = 140 rpm, $n = 3$).

of the biosorption process and subsequently, the removal rate decreased and became uniform after 120 min. As explained by Gupta and Rastogi (2009), initial rapid adsorption probably involves physical adsorption or ion exchange at the cell surface, and the subsequent slower adsorption may involve other mechanisms, such as complexation, microprecipitation, or saturation of binding sites. No significant variation was observed in the percentage of Pb(II) ions removed from the aqueous solution when the suspensions were allowed to stand for 60 min after shaking for 120 min (Figure 4). This indicated that the biosorption process has achieved a well-established equilibrium at 120 min.

The adsorption capacity of *H. verticillata* in comparison with that of other biosorbents reported is shown in Table 1. Among many biosorbents, higher removal of Pb(II) by tea waste (94%) (Amarasinghe and Williams

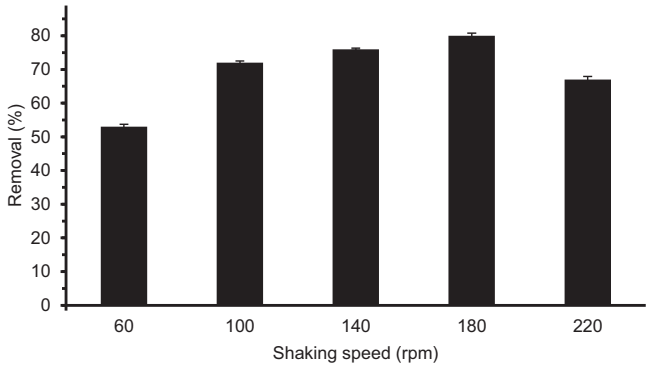

FIGURE 2 Percentage removal of Pb(II) by dry *H. verticillata* biosorbent at different shaking speeds (biosorbent dose = 2.0 g L^{-1}, initial Pb(II) ion concentration = 5.00 mg L^{-1}, pH = 5.0, temperature = 25°C, shaking time = 30 min, $n = 3$).

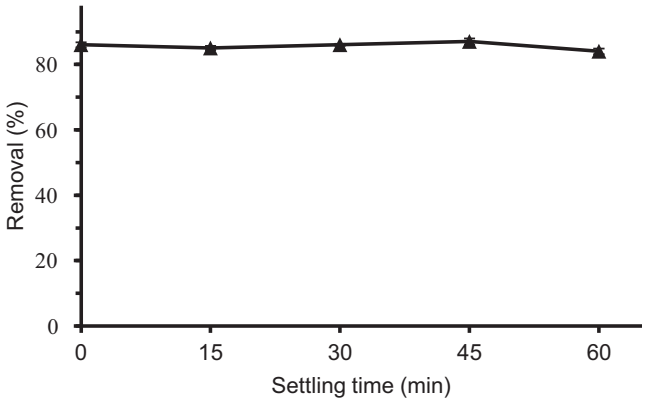

FIGURE 4 Effect of settling time on Pb(II) removal by *H. verticillata* biosorbent after shaking for 120 min (biosorbent dosage = 2.0 g L^{-1}, initial Pb(II) ion concentration = 5.00 mg L^{-1}, pH = 5.0, temperature = 25°C, shaking speed = 140 rpm, $n = 3$).

TABLE 1 Comparison of Pb(II) Adsorption Performance of *H. verticillata* with that of Different Biosorbents

Biosorbent	Sorbent dose (g L^{-1})	Pb(II) concentration (mg L^{-1})	pH	Contact time (min)	Removal capacity (mg g^{-1}) and its percentage	Reference
Tea waste	7.5	100	5.5	90	12.50 (94%)	Amarasinghe and Williams 2007
Ulva lactuca	2.0	10	5.0	60	2.25 (45%)	Sari and Tuzen 2008
H. verticillata	2.0	100	4.0	30	47.00 (94%)	Huang et al. 2009
Chrysophyllum albidium shell	2.0	25	7.0	120	6.90 (55.6%)	Onwu and Ogah 2010
Cystoseira baccata	2.5	414	4.0	50	124.00 (75%)	Lodeiro et al. 2006
Laminaria japonica	1.0	621	5.4	120	248.00 (40%)	Luo et al. 2006
H. verticillata	2.0	5	5.0	120	2.14 (85.7%)	Present study

2007) and by *Cystoseira baccata* (75%) (Lodeiro et al. 2006) were achieved with a high initial metal concentration. In a previous study, Huang et al. (2009) reported that *H. verticillata* removed 94% of Pb(II) from a 100 mg L^{-1} Pb(II) solution. However, the investigation of biosorption performance at lower metal concentrations is also important, as the performance depends on the initial metal concentration. In the present study, *H. verticillata* removed Pb(II) effectively from a solution containing a low metal concentration.

Effect of Biosorbent Dosage

The percentage removal of Pb(II) ions by *H. verticillata* biosorbent at any time increased with the increase in the biosorbent dosage (Figure 3). When the dosage was doubled from 1.0 to 2.0 g L^{-1}, the removal at the equilibrium was increased from 63% to 86%, and when the dosage level was raised up to 4.0 g L^{-1}, 100% removal could be achieved. Similar results were also recorded by previous workers in studies on Pb(II) biosorption (Amarasinghe and Williams 2007; Cabuk et al. 2007). The surface area or the number of adsorption sites available for metal adsorption increases with the increasing biosorbent dosage (Amarasinghe and Williams 2007). However, when the sorbent dose increased from 1.0 to 4.0 g L^{-1}, the maximum mean adsorption capacity of the biosorbent, which was determined using Equation 4, decreased from 3.18 to 1.25 mg g^{-1} (Figure 5). This reduction of the adsorption capacity is due to the fact that at higher adsorbent dose the solution ion concentration drops to a lower value and the system reaches equilibrium at lower values of adsorption capacity, indicating that the adsorption sites remain unsaturated (Amarasinghe and Williams 2007).

$$\text{Mean adsorption capacity} = (C_i - C_f)/\text{biosorbent dosage} \quad (4)$$

Effect of pH

The characteristics of the biosorbent and the nature and the extent of speciation of a metal ion in solution depend on the pH of the solution (Volesky 2003). Therefore, the acidity of the medium is an important parameter among many other factors in biosorption studies (Aksu and Isoglu 2005; Amarasinghe and Williams 2007; Dhakal, Ghimire, and Inoue 2005; Jacques et al. 2007; Mohanty et al. 2006; Sciban, Klasnja, and Skribic 2006, Zhang et al. 2013). Even if the pH was

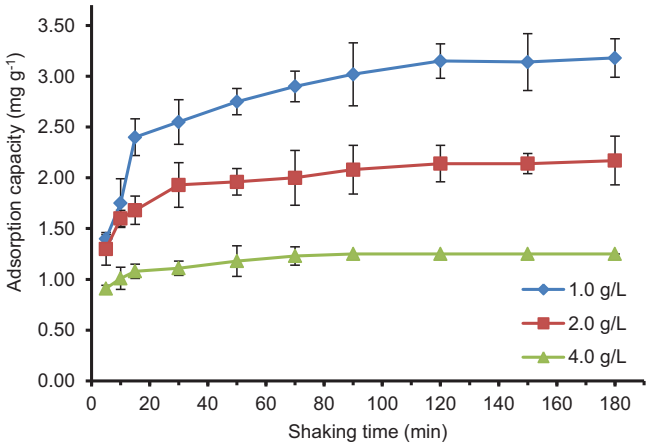

FIGURE 5 Variation of Pb(II) adsorption capacity of *H. verticillata* with time at different biosorbent dosage levels (initial Pb(II) concentration = 5.00 mg L^{-1}, pH = 5.0, temperature = 25°C, shaking speed = 140 rpm, $n = 3$).

properly controlled, the ionic strength and the type of ionic and nonionic constituents would influence the extent of interaction between the ions in solution and the solid biosorbent. Consequently, the effect of solution pH on the extent of removal of ionic species from solution is a complex issue. Therefore, it is important to keep the ionic strength and the type of buffer components unchanged during pH dependent studies.

As depicted in Figure 6, the pH of the medium significantly affected the Pb(II) biosorption potential of *H. verticillata* biomass. The optimum pH for this biosorption process was observed to be 4.0. Pb(II) removal was negligibly low at 3% at pH 2.0. When the pH was raised to 3.0, removal increased to 34%, whereas it increased up to 89% when the pH was 4.0. However, biosorption capacity decreased with further increase in the pH of the medium. This decline was slow from pH 4.0 to 7.0 but accelerated with further increase of the pH. Since the surface of the biosorbent is negatively charged at pH 4.0 (Figure 1), it would have attracted positively charged Pb(II) ions preferably. Further, Pb(II) removal is lower at low pH due to the competition of Pb(II) ions with protons for adsorption sites of the biomass (Huang et al. 2009). Since protons are less bulky than Pb(II) ions, they are more favorably adsorbed on to the surface of the biosorbent.

Although the precipitation of Pb(II) occurs above pH 5.0 (Luo et al. 2006), the amount precipitated is extremely low since the initial concentration of Pb(II) is very low (i.e., 5.00 mg L^{-1} = 2.4×10^{-5} mol L^{-1}). Therefore, this precipitation does not significantly reduce the Pb(II) concentration in the bulk solution. Therefore, the removal rate of Pb(II) does not increase when pHs are higher than 5.0. Since the residual Pb(II) concentration in the bulk solution was measured, this precipitate does not cause a significant error in the final measurements. Hence, biosorption plays the major role in the removal of Pb(II) in the solution. This precipitate may deposit over the surface of the biomass so that it covers the adsorption sites. Hence, the adsorption capacity of the biosorbent is reduced at higher pH. Therefore, the percentage removal of Pb(II) decreases after pH 5.

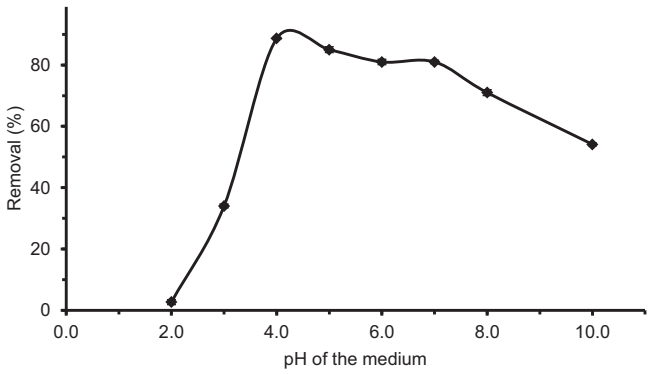

FIGURE 6 **Effect of pH on biosorption of Pb(II) by dry *H. verticillata* biosorbent (biosorbent dosage = 2.0 g L^{-1}, initial Pb(II) ion concentration = 5.00 mg L^{-1}, temperature = 25°C, shaking time = 120 min, shaking speed = 140 rpm, $n = 3$).**

FT-IR Analysis of the Biosorbent

The functional groups on the biosorbent surface responsible for the Pb(II) binding process were determined by comparing the FT-IR spectra of the biosorbent obtained before and after biosorption (Figure 7). The FT-IR spectrum of *H. verticillata* consisted of many vibrational bands, indicating that the surface of the *H. verticillata* biosorbent is complex in nature with various functional groups. Certain intense characteristic peaks in the spectrum arose due to the functional groups presented in proteins and polysaccharides in the biosorbent (Huang et al. 2010).

According to Table 2, spectral peak positions corresponding to bonded O—H and C=O stretching of acylamide has shifted to lower frequencies significantly by 27 and 15 cm^{-1}, respectively. This shifting of peak positions suggested that hydroxyl and C=O of acylamide functional groups on the biosorbent surface combined with Pb(II) ions. Huang et al. (2010) reported a similar result obtained for Cd(II) biosorption by *H. verticillata*.

Kinetics of the Adsorption Process

Evaluation of kinetic parameters of a biosorption process is useful for designing a adsorption system and to determine the controlling mechanism of the adsorption process. The adsorption kinetics of a system are controlled by different steps, including transfer of solute to the sorbent particle surface, transfer from the sorbent surface to the intraparticle active sites, and retention on these active sites via adsorption, complexation, or intraparticle precipitation phenomena (Shroff and Vaidya 2011). Hence, the experimental data were tested with three different kinetic models: pseudo-first-order model, pseudo-second-order model, and intraparticle diffusion model.

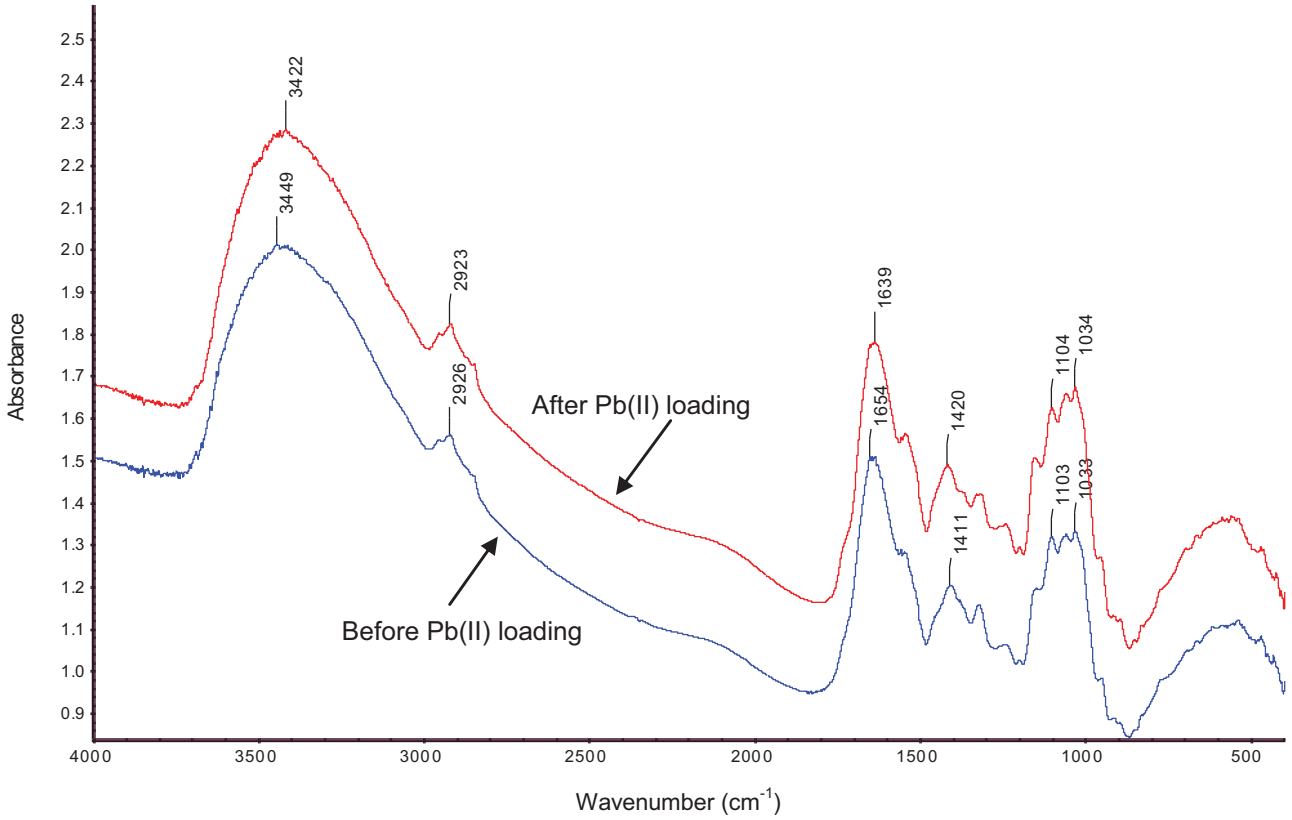

FIGURE 7 **FT-IR spectra of the *H. verticillata* biosorbent before and after contact with Pb(II) ion solutions.**

Order of the Biosorption Process

Amounts of Pb(II) ions adsorbed by *H. verticillata* biosorbent at different times in time course experiments were tested against the pseudo-first-order kinetic model (Equation 5) and the pseudo-second-order kinetic model (Equation 6) to determine the order of the biosorption process.

$$\ln(q_e - q_t) = -k_1 t + \ln q_e \quad (5)$$

$$1/q_t = 1/(k_2 q_e^2 t) + 1/q_e \quad (6)$$

where q_e and q_t denote the amounts of metal ions adsorbed per unit mass of the sorbent (mg g^{-1} dry biomass) at equilibrium and at time t, respectively, whereas k_1 and k_2 are the pseudo-first-order rate constant (min^{-1}) and the pseudo-second-order rate constant (g mg^{-1} min^{-1}), respectively. The amount of metal ions adsorbed on to biosorbent was calculated by using Equation 7 (Jacques et al. 2007):

$$q = (C_0 - C_f)\,V/m \quad (7)$$

where q is the amount of metal ion adsorbed by the biosorbent (mg g^{-1} dry biomass), C_0 is the initial metal ion concentration (mg L^{-1}), C_f is the metal ion concentration (mg L^{-1}) after biosorption process, V is the

TABLE 2 **FT-IR Spectral Bands in the *H. verticillata* before and after Contact with Pb(II) Solution**

FT-IR band wavenumber (cm^{-1})			
Before Pb(II) removal	After Pb(II) removal	Functional group assignment	Reference
3449	3422	Bonded O—H	Jacques et al. 2007; Huang et al. 2010
2926	2923	Methylene asymmetric C—H stretching	Pavia et al. 2009
1654	1639	C=O stretching of acylamide	Pavia et al. 2009; Huang et al. 2010
1411	1420	C—N stretching of amides	Pavia et al. 2009
1103	1104	C—OH stretching of alcohols	Jacques et al. 2007
1033	1034	C—O stretching of ethers	Netzahuatl-Muñoz et al. 2012

TABLE 3 Comparison of Pseudo-First-Order and Pseudo-Second-Order Kinetic Parameters of Biosorption of Pb(II) by *H. Verticillata*

		Pseudo-first-order model			Pseudo-second-order model		
Dose (g L^{-1})	q_e (experimental) (mg g^{-1})	k_1 (min^{-1})	q_e (calculated) (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_e (calculated) (mg g^{-1})	R^2
1.0	3.15	0.027	1.91	0.957	0.041	3.78	0.966
2.0	2.14	0.027	0.86	0.934	0.126	2.52	0.990
4.0	1.25	0.036	0.44	0.968	0.406	1.45	0.956

Note. Initial metal ion concentration = 5.00 mg L^{-1}, pH = 5.0, temperature = 25°C, shaking speed = 140 rpm.

volume (L) of metal ion solution kept in contact with the biosorbent, and m is the mass (g) of biosorbent.

The experimental data were plotted under each model and the corresponding kinetic parameters were evaluated from the slopes and intercepts of the plots. The values of rate constants (k_1 and k_2) and q_e obtained under each model at different dose levels are presented in Table 3, along with their relevant regression coefficients (R^2). Although there was no significant difference between R^2 values obtained under each model, the experimental q_e value is closer to the q_e value calculated from the pseudo-second-order model (Table 3). Hence, considering both factors (i.e., R^2 values and q_e values), the adsorption of Pb(II) ions on to the nonliving *H. verticillata* biomass is assumed to follow pseudo-second-order kinetics, indicating that the rate of the biosorption process depends on both the Pb(II) concentration and the concentration of biosorbent (Jacques et al. 2007; Shroff and Vaidya 2011). Further, the pseudo-second-order rate constant (k_2) increased with increasing sorbent dosage, as reported in many other previous publications (Du, Lian, and Zhu 2011; Jacques et al. 2007; Mohanty et al. 2006; Prahas et al. 2008; Rao, Khan, and Rehman 2010; Shroff and Vaidya 2011; Vinod, Sashidhar, and Sreedhar 2010).

Intraparticle Diffusion Model

The basic assumption of the intraparticle diffusion model is that the film diffusion is negligible and intraparticle diffusion is the only rate-controlling step (Mohan et al. 2007). The compatibility of adsorption data obtained for this biosorption with the intraparticle diffusion model was determined using Equation 8.

$$q_t = k_i\, t^{0.5} \tag{8}$$

where q_t is the amount of Pb(II) adsorbed per unit mass of sorbent (mg g^{-1}) at time t (mg g^{-1}), and k_i is the intraparticle rate constant (mg g^{-1} $min^{-0.5}$). Since the plot of q_t versus $t^{0.5}$ does not pass through the origin (Figure 8), the intraparticle diffusion is not the only rate-controlling step for adsorption of aqueous Pb(II) on to the surface of nonliving *H. verticillata* biomass (Mohan et al. 2007; Mohanty et al. 2006; Shroff and Vaidya 2011).

Effect of Initial Metal Concentration and Adsorption Isotherms

Analysis of the adsorption equilibrium data is important for designing of a biosorption system (Srividya and Mohanty 2009). Figure 9 shows that the concentration of Pb(II) remained at the equilibrium (C_e) increased with the increase of the initial Pb(II) concentration in biosorption medium. The adsorption isotherm obtained for the Pb(II) biosorption process is shown in Figure 10, and the isothermal data were tested with the Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) isotherm models.

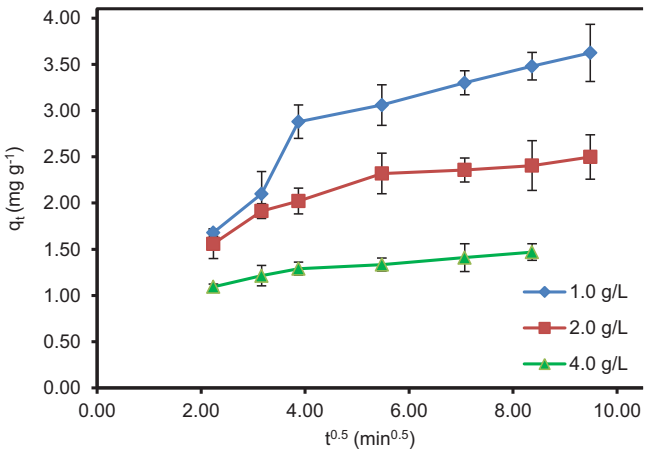

FIGURE 8 Intraparticle diffusion for Pb(II) adsorption onto *H. verticillata* biomass (initial Pb(II) ion concentration = 5.00 mg L^{-1}, pH = 5.0, temperature = 25°C, shaking speed = 140 rpm, n = 3).

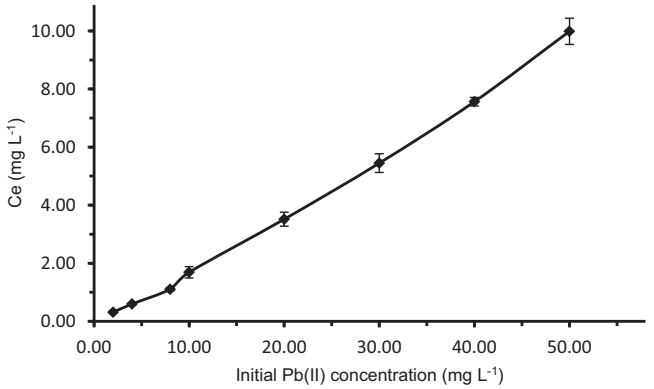

FIGURE 9 **Variation of Pb(II) concentration at equilibrium with initial Pb(II) concentration in the biosorption medium (biosorbent dosage = 2.0 g L^{-1}, pH = 5.0, temperature = 25°C, shaking speed = 140 rpm, $n = 3$).**

The linear form of the Langmuir isotherm model (Langmuir 1916) is given by

$$1/q_e = 1/bq_0C_e + 1/q_0 \tag{9}$$

where q_e is the amount of metal ions adsorbed per unit mass of the sorbent (mg g^{-1} dry biomass) at equilibrium, b is the adsorption coefficient, q_0 is the amount of metal ions adsorbed per unit mass of the sorbent (mg g^{-1} dry biomass) corresponding to complete coverage of available sites (i.e., monolayer saturation capacity), and C_e is the residual metal ion concentration (mg L^{-1}) at equilibrium. The values of b and q_0 were evaluated from the slope and intercept of the linear plot of $1/q_e$ versus $1/C_e$, respectively.

The Freundlich isotherm model (Mohanty et al. 2006) is expressed as

$$\ln q_e = \ln k + 1/n \ln C_e \tag{10}$$

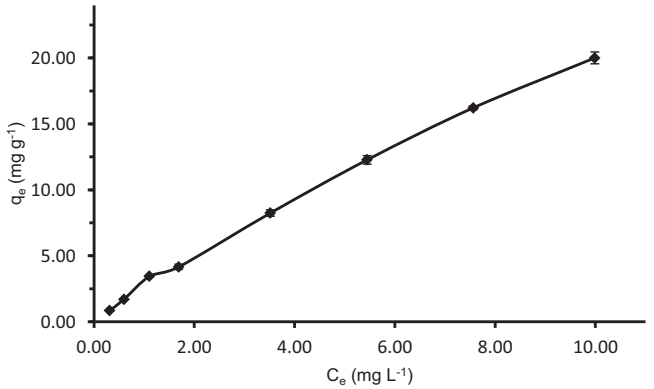

FIGURE 10 **Adsorption isotherms for Pb(II) adsorption onto *H. verticillata* biomass (biosorbent dosage = 2.0 g L^{-1}, pH = 5.0, temperature = 25°C, shaking speed = 140 rpm, $n = 3$).**

where k and n are the constants related to adsorption capacity and adsorption intensity, respectively. These constants were determined from the intercept and slope of the linear plot of ln q_e versus ln C_e, respectively.

Higher R^2 values suggested that the experimental data fitted to both Langmuir and Freundlich isotherms under the given adsorption conditions. The isotherm constants and the R^2 values are given in Table 4. Results of the Langmuir isotherm model were further analyzed using Equation 11.

$$R_L = 1/(1 + bC_0) \tag{11}$$

where R_L is the adsorption intensity which has four probabilities: (1) $0 < R_L < 1$, favorable adsorption; (2) $R_L > 1$, unfavorable adsorption; (3) $R_L = 1$, linear adsorption; and (4) $R_L = 0$, irreversible adsorption (Huang et al. 2010). The R_L value of the biosorption of Pb(II) onto *H. verticillata* ranges from 0.47 to 0.95, indicating that the adsorption process is favorable when the initial Pb(II) concentration ranged from 2 to 50 mg L^{-1}. Moreover, the low value of $1/n$ (<1) evaluated from Freundlich model also confirmed that adsorption is favorable (Du et al. 2011, Huang et al. 2010).

The nature of the adsorption (i.e., physical or chemical) is determined by the D-R isotherm model whose linear form of the model (Huang et al. 2010) is expressed by Equation 12.

$$\ln q_e = \ln q_0 - \beta\varepsilon^2 \tag{12}$$

where β is the activity coefficient related to mean adsorption energy (mol^2 J^{-2}) and ε is the Polanyi potential which is calculated by Equation 13.

$$\varepsilon = RT \ln(1 + 1/C_e) \tag{13}$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature (K). The mean

TABLE 4 **Adsorption Isotherm Constants for the Biosorption of Pb(II) by *H. verticillata***

Langmuir model	Freundlich model	D-R model
$R^2 = 0.996$	$R^2 = 0.995$	$R^2 = 0.804$
$q_0 = 125$ mg g^{-1}	$k = 2.664$	$q_0 = 10$ mg g^{-1}
$b = 0.022$ L mg^{-1}	$1/n = 0.896$	$\beta = 2 \times 10^{-7}$ mol^2 J^{-2}

Note. Biosorbent dosage = 2.0 g L^{-1}, pH = 5.0, temperature = 25°C, shaking speed = 140 rpm.

adsorption energy, E (kJ mol^{-1}), can be determined using Equation 14.

$$E = 1/\sqrt{2\beta} \quad (14)$$

The values of β and q_0 were calculated from the slope and the intercept of the plot of ln q_e versus ε^2 and are given in Table 4. The mean adsorption energy (E) of the biosorption process was calculated as 1.58 kJ mol^{-1}. Since $E < 8$ kJ mol^{-1}, the adsorption is physical in nature (Huang et al. 2010). However, Huang et al. (2009) reported that the adsorption of Pb(II) on to *H. verticillata* followed a chemical ion-exchange mechanism at higher Pb(II) concentrations.

Desorption of Pb(II) from Metal-Loaded Biomass

Out of the four desorbing solutions tested, nitric acid showed the best performance (Table 5). Although nitric acid at pH 1 gave 100% desorption, it damaged the biosorbent. In contrast, basic media did not favor the desorption process. Among the two sodium salts tested, Na_2CO_3 showed better performance over $NaNO_3$. When the metal-loaded biomass is exposed to a desorbing solution, the metal is detached from the substrate either through precipitation, complexation, or ion-exchange mechanism (Gardea-Torresdey, Rosa, and Peralta-Videa 2004). HNO_3 and NaOH medium supports the ion-exchange mechanism, whereas the Na_2CO_3 medium supports the complexation mechanism (Gardea-Torresdey, Rosa, and Peralta-Videa 2004). The reduction in desorption percentage with the increase in pH in NaOH solution may be due to the precipitation of Pb(II) released into the solution as Pb$(OH)_2$, which is removed during filtration. Hence, the amount of Pb determined by the AAS analysis of the filtrate is less than the total amount of Pb released into the desorption solution. The loss of Pb(II) due to precipitation became greater with the increase in pH and resulted in lower desorption percentages. Although nitric acid gave better results, it is more suitable to use Na_2CO_3 to recover Pb(II), since it is less expensive and environmentally less harmful.

TABLE 5 Percentage of Pb Desorbed Using Different Desorbing Agents

Desorbing agent	pH/concentration of desorbing solution	Desorption (%)
HNO_3	pH = 1	100
	pH = 2	92
	pH = 3	56
NaOH	pH = 10	14
	pH = 11	11
	pH = 12	12
Na_2CO_3	0.05 mol L^{-1}	2
	0.10 mol L^{-1}	8
	0.50 mol L^{-1}	40
$NaNO_3$	0.05 mol L^{-1}	0
	0.10 mol L^{-1}	4
	0.50 mol L^{-1}	7

CONCLUSIONS

Nonliving biomass of *H. verticillata* effectively removed Pb(II) from the aqueous solution containing a very low Pb(II) concentration. The maximum percentage removal of Pb(II) was obtained at the equilibrium point, and it increased with the increasing adsorbent dosage. The optimum pH of the biosorption was 4.0. The surface of the biosorbent was positively charged at low pH and negatively charged at pH above 3.6. FT-IR spectra showed that hydroxyl and C=O of acylamide functional groups on the biosorbent surface were involved in the Pb(II) adsorption process. Kinetics of the adsorption processes followed the pseudo-second-order kinetic model, whereas their equilibrium data followed both Langmuir and Freundlich adsorption isotherms. The mean adsorption energy showed that the adsorption of Pb(II) was physical in nature. Good desorption of Pb(II) from the biosorbent was shown by HNO_3 and Na_2CO_3.

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