

# Treatment of Pb ion contaminated wastewater using hazardous parthenium (*P. hysterophorus* L.) weed

Kulbhushan Samal, Kaustubha Mohanty and Chandan Das

## ABSTRACT

In this study, a low-cost, sustainable biosorbent parthenium (*P. hysterophorus* L.) weed powder was investigated for the treatment of Pb contaminated wastewater. Physicochemical characteristics of the biosorbent were measured, namely, bulk density as  $0.42 \text{ g cm}^{-3}$ , porosity as 45%, BET surface area as  $20.79 \text{ m}^2 \text{ g}^{-1}$ , particle size as  $<125 \mu\text{m}$ , moisture content as 68% and point of zero charge as 5.6. The various parameters of biosorption process were examined. The maximum percentage removal of Pb ion achieved was 98.3% with  $1.0 \text{ g L}^{-1}$  of biosorbent dose for  $50 \text{ mg L}^{-1}$  initial Pb ion concentration at process condition of pH 4, temperature  $30 \text{ }^\circ\text{C}$  (303 K), agitation speed 200 rpm and 150 min of equilibrium contact time. The equilibrium data were examined by various rate kinetics models and adsorption isotherm models. Sorption of Pb ion onto biosorbent was confirmed by Fourier transform infrared spectroscopy (FTIR) transmittance spectra and field-emission scanning electron microscopy and energy-dispersive X-ray (FESEM-EDX) analysis of native as well as Pb ion adsorbed biosorbent. The change in thermodynamic parameters, such as Gibbs free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) was calculated. The results suggest that biosorption process using parthenium (*P. hysterophorus* L.) weed powder as biosorbent was a spontaneous, feasible and efficient method for treatment of Pb-bearing wastewater.

**Key words** | biosorption, isotherms, kinetics, lead, parthenium, wastewater

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## NOMENCLATURE

|       |  |       |   |
|-------|--|-------|---|
| $1/n$ | Freundlich model constants related to intensity of adsorption                    | $K''$ | Pseudo-second-order rate constant of biosorption in $\text{mg g}^{-1} \text{ min}^{-1}$     |
| $B$   | Constant related to adsorption energy $E$ in $\text{mol}^2 \text{ kJ}^{-2}$      | $K_d$ | Distribution coefficient  |
| $E$   | Free energy of adsorption in $\text{kJ mol}^{-1}$                                | $K_F$ | Freundlich model constants related to adsorption capacity                                   |
| $e$   | Polanyi potential  | $K_L$ | Langmuir biosorption constant in $\text{L mg}^{-1}$ relating the free energy of biosorption |
| $q$   | Metal uptake capacity in $\text{mg g}^{-1}$                                      | $K_p$ | Intra-particle diffusion rate constant in $\text{mg g}^{-1} \text{ min}^{-1/2}$             |
| $R$   | Gas constant in $\text{kJ mol}^{-1} \text{ K}^{-1}$                              | $q_e$ | Equilibrium metal uptake capacity in $\text{mg g}^{-1}$                                     |
| $T$   | Temperature in K   | $q_m$ | Monolayer biosorption capacity of the biosorbent in $\text{mg g}^{-1}$                      |
| $V$   | Volume of the solution in L  | $R_L$ | Dimensionless constant separation factor  |
| $W$   | Mass of biosorbent in g  | $S$   | Entropy in $\text{kJ mol}^{-1}$   |
| $C_e$ | Equilibrium metal ion concentration in solution $\text{mg L}^{-1}$               |       |   |
| $C_o$ | Initial metal ion concentration in $\text{mg L}^{-1}$                            |       |   |
| $C_a$ | Equilibrium metal ion concentration adsorbed on adsorbent in $\text{mg L}^{-1}$  |       |   |
| $G$   | Gibbs free energy in $\text{kJ mol}^{-1}$  |       |   |
| $H$   | Enthalpy in $\text{J mol}^{-1}$  |       |   |
| $K'$  | First-order Lagergren kinetics rate constant of biosorption in $\text{min}^{-1}$ |       |   |

## INTRODUCTION

In the last two decades, there is a continuously growing interest of researchers in developing new techniques and materials

for removal of hazardous pollutants from wastewater. Among the water pollutants, heavy metals, in particular, Pb is more dangerous due to its toxic nature to human being (Mishra & Patel 2009). This Pb ion contamination is mainly originated from various industrial activities, fuel refining and use, metallurgy, pigmenting, etc. (Volesky & Holan 1995). The presence of Pb ion in the human body can cause anemia, gastrointestinal, cardiovascular, nervous, and memory diseases mainly in children and pregnant women. The maximum permissible limit of Pb ion concentration in drinking water set by the European community and the World Health Organization (WHO) is  $0.05 \text{ mg L}^{-1}$  (Gupta & Rastogi 2008).

The conventional methods used for treating Pb ion contaminated wastewater includes physical processes, such as UV radiation, filtration and membrane process, etc. The chemical processes, namely chlorine, ozone, iodine treatment, etc. and physicochemical processes, such as ion exchange, chemical coagulation and precipitation, etc. have been used (Gupta & Ali 2004). Although these techniques have their advantages, they also have different disadvantages, such as inefficient removal of metal ion, the requirement of expensive chemicals, not practicable and sometimes cause secondary pollution. Another physicochemical process, adsorption process is one of the efficient methods studied extensively (Ghaedi et al. 2016; Mazaheri et al. 2016). But high adsorbents price and the requirement of adsorbent regeneration step make this process inadequate.

In recent years, the living and nonliving biomass of biological materials have received considerable attention due to their binding ability of heavy metal ions (Jianlong et al. 2001). Literature survey reveals that biosorption process was studied extensively for removal or recovery of heavy metal ions from wastewater using several biological materials as an adsorbent. The range of biomass as biosorbent is wide including husk, bark, leaves, aquatic plants, algae, animal bone, fungi, bacteria, yeast, etc. (Gupta & Ali 2004; Asfaram et al. 2016). The significant advantages of biosorption process over other conventional treatment techniques include inexpensive materials, derived from renewable sources, easy availability, high removal efficiency of pollutants, no requirement of adsorbent regeneration, and possibility of metal recovery.

The biomass of parthenium (*P. hysterophorus* L.), a native of Mexico and now widely spread in Australia, China, Pacific Islands, India, and the subcontinent, has recently drawn the attention of researchers due to its hazardous nature and harmful effect on human beings. Prolonged exposure of parthenium (*P. hysterophorus* L.) weed may cause several health issues in people, such as asthma, eczema, hay fever, black spots, blisters around eyes, and

burning. This species is amply available and has no economical use. Only a few studies found reporting the utilization of parthenium were, as a biosorbent for Cr (VI) ion sorption (Venugopal & Mohanty 2011), Cd (II) ion sorption in aqueous solution (Ajmal et al. 2006). The weed was also studied in the production of biofuels (Singh et al. 2015).

In this study, the waste biomass of parthenium (*P. hysterophorus* L.) weed was investigated as biosorbent for Pb ion sorption in aqueous solution. First, the biosorbent was developed from waste biomass of parthenium (*P. hysterophorus* L.) and their physicochemical characteristics such as bulk density, porosity, Brunauer–Emmett–Teller (BET) surface area, particle size, moisture content, point of zero charge, Fourier transform infrared spectroscopy (FTIR) transmittance spectra, field-emission scanning electron microscopy and energy-dispersive X-ray (FESEM-EDX) spectra were analyzed. Next, the batch biosorption experiments were conducted to evaluate the effect of contact time, initial Pb ion concentration, adsorbent dose, pH, agitation speed and temperature on Pb ion uptake. Then, the Pb ion sorption kinetic studies were carried out by fitting the biosorption experimental data with the pseudo-first-order kinetic model, pseudo-second-order model, and Weber–Morris model. Finally, the equilibrium data were tested with three isotherm models (viz. Langmuir, Freundlich, and Dubinin–Radushkevich (D-R)) and the thermodynamics parameters, such as Gibbs free energy (G), enthalpy (H), and entropy (S) were evaluated.

## MATERIALS AND METHODS

### Preparation of biosorbent

Parthenium (*P. hysterophorus* L.) weed was collected from inside IIT Guwahati campus. The adhering impurities and dust were removed from plants surface by cleaning it with tap water. Then, those were dried naturally in sunlight for one week, then in hot air oven (Sonuu Instruments, India) at  $70^\circ\text{C}$  (343 K) for 24 h. Next, the dried weeds were ground into fine powder in mixer grinder (Bajaj, mixer grinder, India). Powdered biosorbent was sieved through 120 BSS mesh screen (particle size:  $125 \mu\text{m}$ ) (Multi Science, India) and then the powdered biosorbent was stored in zip-ping lock plastic bags for further applications.

### Stock solution preparation

A synthetic wastewater stock solution of  $1,000 \text{ mg L}^{-1}$  Pb ion concentration was made in the laboratory by dissolving

1.606 g of lead nitrate (minimum purity 99.5%, Merck, Germany) in approximately 250 mL of deionized water. 10 mL of 0.1 M HNO<sub>3</sub> (Merck, Germany) was added and diluted to 1,000 mL with deionized water. This stock solution was used after further dilution with deionized water; the required solutions concentrations were ranging between 20 and 200 mg L<sup>-1</sup>. All the chemicals and reagents used in these studies were of analytical grade and used without any further purification.

### Analysis of physicochemical characteristics of biosorbent

The physicochemical properties of biosorbent parthenium (*P. hysterophorus* L.) such as bulk density, porosity, BET surface area (Coulter, SA3100, Germany) were measured. Also, the particle size (Mastersizer, APA 2000, UK), moisture content and point of zero charge (Beckman Coulter, Delsa<sup>TM</sup> Nano C, Germany) were analyzed. The bulk density of developed biosorbent was measured as 0.42 g cm<sup>-3</sup>, porosity as 45%, BET surface area as 20.79 m<sup>2</sup> g<sup>-1</sup>, particle size as <125 μm, moisture content as 68% and point of zero charge as 5.6. The pH value of the biosorbent dispersed solution was measured using Eutech Instruments, pH700, India. The FTIR transmittance spectra (Shimadzu, IR Affinity-1, Japan) of both native as well as Pb ion loaded biosorbent were analyzed using KBr (Merck KGaA, Germany) matrix. The elemental composition of native, as well as Pb ion, adsorbed biosorbent were analyzed by FESEM-EDX (Zeiss, Sigma, USA) analysis.

### Batch biosorption experiments

All the batch sorption experiments were carried out in conical flasks (250 mL). To evaluate equilibrium contact time of biosorption process an equal amount (1.0 g L<sup>-1</sup>) of dry native biosorbent was mixed with 200 mL of the solution having different initial Pb ion concentrations (20, 50, 70, 100, 150 and 200 mg L<sup>-1</sup>). The measured natural pH value of the solution was found to be 2.6. This solution was shaken at 200 rpm rotational speed using an incubator shaker (Daihan LabTech, LSI-3016R, India) at room temperatures (303 ± 2 K). At different time intervals, viz. 10, 20, 40, 60, 90, 120, 150 and 180 min, a 5 mL volume of solution were taken out using a dispensary syringe (Hindustan Syringes, India) from the respective solutions. Then, it was filtered through Whatman No. 1 filter paper (O Sicerin & Biva, India). First, 1 mL of filtrate was discarded to avoid the possibility of adsorption by filter paper. The rest

volume of filtrates was diluted 10-fold and then analyzed by using atomic absorption spectrometer (Varian, AA240AS, The Netherlands) for determining the residual Pb ion concentration in the solution. The standard method for Pb ion analysis prescribed in ASTM-D3559 was followed. Next, in order to investigate the effect of biosorbent dose on Pb ion uptake, a dose of 0.2, 0.4, 0.6, 0.8 and 1.0 g L<sup>-1</sup> of native biosorbent was used for Pb ion solution having the concentration of 50 and 100 mg L<sup>-1</sup>. The effects of other parameters, such as solution pH (at the pH value of 2, 2.6, 4, 5 and 6), temperature (at 293, 303, 313 and 323 K) and rotational speed (50, 100, 150, 200 and 250 rpm) were investigated. For these experiments, three different initial Pb ion concentrations 50, 100 and 150 mg L<sup>-1</sup> and an optimum biosorbent dose 1.0 g L<sup>-1</sup> was used. The average value of three replicate were taken and the % error was less than ±3.5% of the average value.

*Metal uptake and percentage sorption:* The metal uptake and % sorption were calculated according to Equations (1) and (2), respectively:

$$q = \frac{(C_o - C_e)V}{W} \quad (1)$$

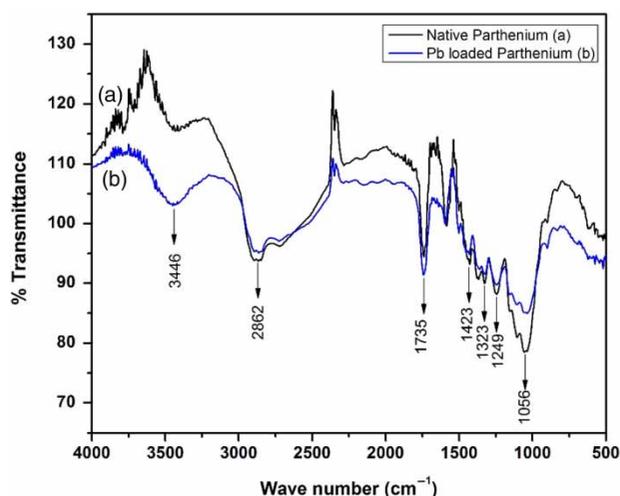
$$\text{Sorption \%} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

where  $q$  is equilibrium metal uptake capacity in mg g<sup>-1</sup>,  $C_o$  is initial metal ion concentration in mg L<sup>-1</sup>,  $C_e$  is equilibrium metal ion concentration in mg L<sup>-1</sup>,  $V$  is the volume of the solution in L and  $W$  is the mass of biosorbent in g.

## RESULTS AND DISCUSSION

### Spectral analysis of biosorbent

The FTIR transmittance spectra of both native, as well as Pb ion loaded biosorbent were analyzed to detect the various chemical functional groups present on adsorbent surfaces, which were responsible for Pb ion binding. The transmittance spectra were recorded within the range of 500–4,000 cm<sup>-1</sup> wave number. Figure 1 shows FTIR transmittance spectra of both the adsorbents (native as well as Pb ion loaded parthenium (*P. hysterophorus* L.)). The major shift in peaks observed from FTIR transmittance spectra of biosorbents was at 3,446 cm<sup>-1</sup> correspond to unbounded –OH group and 2,862 cm<sup>-1</sup> represents the majority of the aliphatic fraction. The peak at 1,735 cm<sup>-1</sup> is associated



**Figure 1** | FTIR transmittance spectra of native and Pb loaded parthenium (*P. hysterophorus* L.).

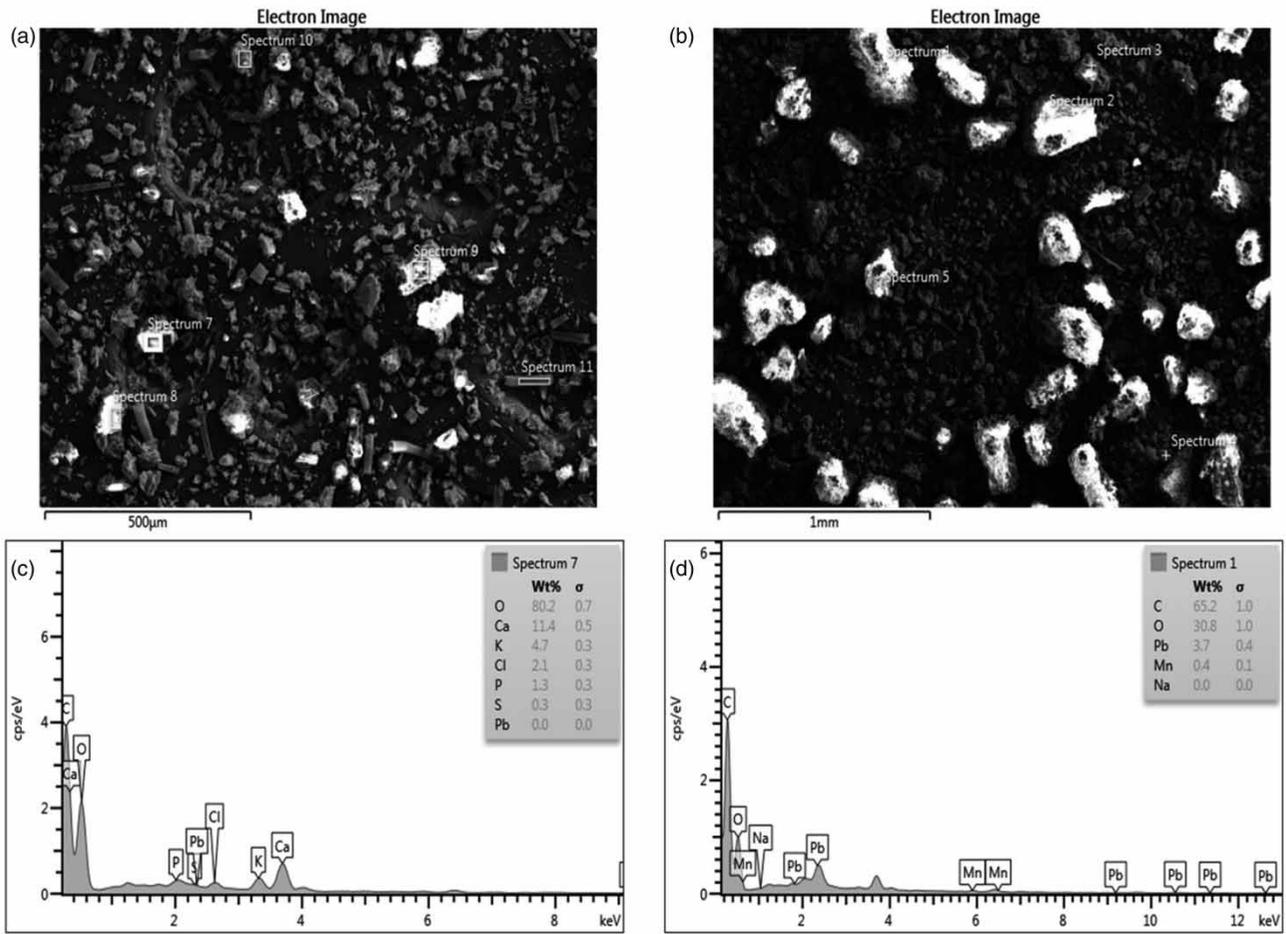
with C-X group, and  $1,423\text{ cm}^{-1}$  indicates the presence of C-F group,  $1,323\text{ cm}^{-1}$  shows C-N stretching vibration, which corresponds to the amine groups. The peak at  $1,249\text{ cm}^{-1}$  is due to C=O deformation vibration and -OH stretching indicates the presence of aliphatic acid group and  $1,056\text{ cm}^{-1}$  associated with C-O-C functional groups (Coates 2000). The significant change in peaks and intensity of FTIR transmittance spectra confirmed that various functional group such as -OH, C-X, C-F, C-N and C=O groups were the main responsible functional groups for Pb ion sorption present on biosorbent. These functional groups of biosorbent provide active sites for complex formation with the metal ion and some coordination bonds might have formed between them. However, the metal uptake depends on various other factors, such as availability and accessibility of active sites, the affinity between the site and the metal ion. The biosorption of Pb ions on the biosorbent may happen through various mechanisms, such as ion exchange, physical sorption, chemisorption and complexation (Pholosi et al. 2013; Asfaram et al. 2016). The biosorption of Pb ion on biosorbent was also confirmed by FESEM-EDX analysis of native and Pb ion adsorbed biosorbent. The FESEM images of native and Pb ion adsorbed parthenium (*P. hysterophorus* L.) are shown in Figure 2(a) and 2(b), whereas Figure 2(c) and 2(d) show their EDX spectra respectively. In the elemental analysis of native and Pb ion loaded adsorbent, EDX spectra of Pb ion loaded biosorbent (Figure 2(d)) was showing peaks for Pb, which was absent in EDX spectra of native biosorbent (Figure 2(c)). It suggests that Pb ions were adsorbed on biosorbent surface during the biosorption process.

### Effect of contact time and initial Pb ion concentration

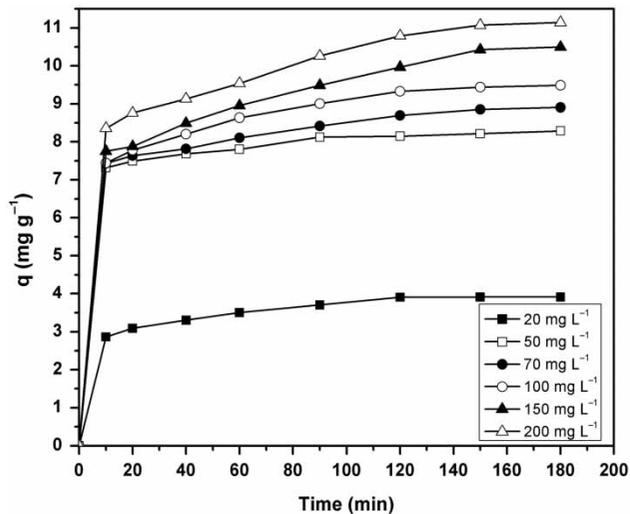
To investigate the effect of contact time and initial Pb ion concentration on adsorption of Pb ions, experiments were performed in incubator shaker using various initial Pb ion concentrations of 20, 50, 70, 100, 150 and  $200\text{ mg L}^{-1}$  at natural pH of 2.6. An equal amount of biosorbent  $1.0\text{ g L}^{-1}$  was added to the solution at room temperature ( $303 \pm 2\text{ K}$ ) and agitation speed was maintained at 200 rpm. Samples at different time intervals viz. 10, 20, 40, 60, 90, 120, 150 and 180 min were taken out, and Pb ion concentration was analyzed. The metal uptake as a function of contact time is shown in Figure 3, which clearly indicates that metal uptake was increased up to 150 min of biosorption process after that uptake remained almost constant, which shows that, an equilibrium between adsorbate and adsorbent was attained after 150 min. Figure 4 illustrates the effect of initial Pb ion concentration in solution on metal uptake and percentage removal Pb ion. The higher percentage removal was observed at lower initial Pb ion concentration because the surface of a fix amount of biomass can adsorb a certain amount of metal ion at equilibrium. The percentage removal of Pb ion were 97.8%, 82.2% and 27.6% for initial Pb ion concentration of  $20\text{ mg L}^{-1}$ ,  $50\text{ mg L}^{-1}$  and  $200\text{ mg L}^{-1}$ , respectively, which indicates that the biosorption process was efficient on the lower metal to the biosorbent ratio in the solution ( $<0.05$ ). The higher uptake value was observed at higher initial Pb ion concentration due to the higher Pb ion to biosorbent ratio in solution at equilibrium.

### Effect of biosorbent dose

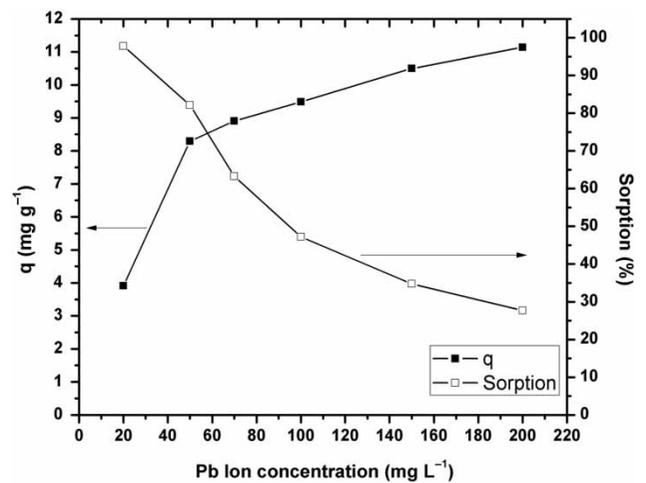
The biosorption experiments were performed to find out the effect of biosorbent dose on Pb ion uptake and percentage removal, with taking initial Pb ion concentration of  $50\text{ mg L}^{-1}$  and adsorbent dose from  $0.2\text{ g L}^{-1}$  to  $1.0\text{ g L}^{-1}$  at its natural pH 2.6. In this experiment, 200 rpm agitation speed at room temperature ( $303 \pm 2\text{ K}$ ) was maintained for 150 min. It can be seen from Figure 5 that, with increasing the biosorbent dose, percentage removal of Pb ion by parthenium (*P. hysterophorus* L.) increased from 69.72% to 82.9% for initial Pb ion concentration of  $50\text{ mg L}^{-1}$ . The increase in percentage removal of Pb ion was due to the increase of active surface area with increasing biosorbent dose and decreasing metal ion to biosorbent ratio in solution. However, the uptake capacity of Pb ion decreased from  $32.14\text{ mg g}^{-1}$  to  $8.132\text{ mg g}^{-1}$  for initial Pb concentration of  $50\text{ mg L}^{-1}$ . The decrease in metal uptake value ( $q$ ) with increasing biosorbent dose was because the metal to biosorbent ratio in solution



**Figure 2** | FESEM image and EDX spectra of native and Pb loaded parthenium (*P. hysterophorus* L.): (a) FESEM image of native adsorbent; (b) FESEM image of Pb ion loaded adsorbent; (c) EDX spectra of native adsorbent; (d) EDX spectra of Pb ion loaded adsorbent.



**Figure 3** | Effect of contact time on metal uptake (pH: 2.6; biosorbent dose:  $1.0 \text{ g L}^{-1}$ ; agitation speed:  $200 \text{ rpm}$ ; temperature:  $30 \pm 2 \text{ }^\circ\text{C}$  ( $303 \pm 2 \text{ K}$ )).



**Figure 4** | Effect of initial Pb ion concentration on metal uptake and percentage removal (pH: 2.6; biosorbent dose:  $1.0 \text{ g L}^{-1}$ ; contact time: 150 min; agitation speed:  $200 \text{ rpm}$ ; temperature:  $30 \pm 2 \text{ }^\circ\text{C}$  ( $303 \pm 2 \text{ K}$ )).

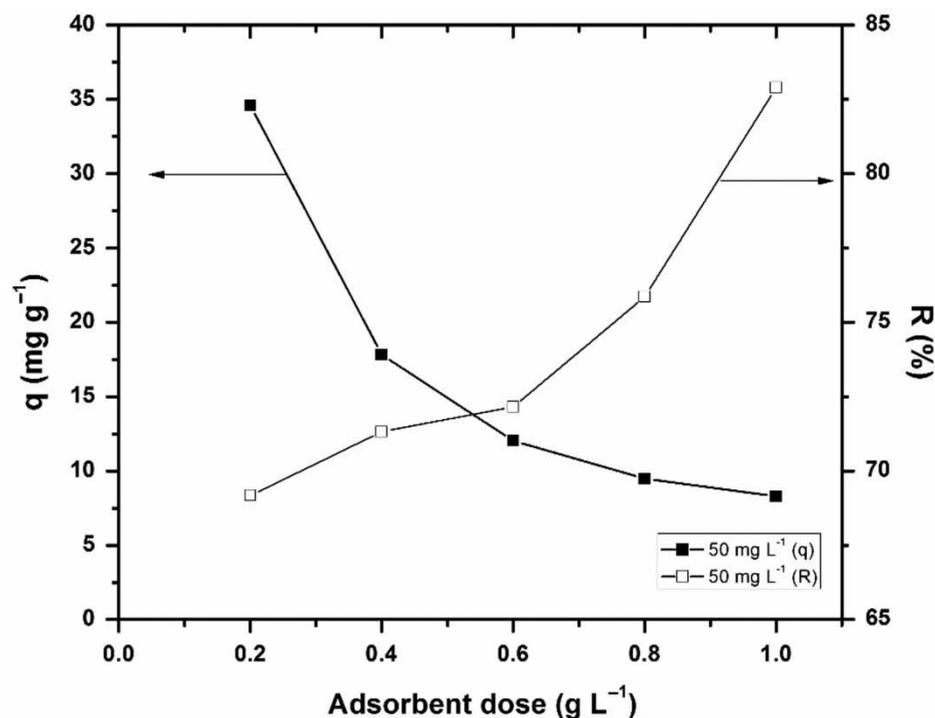


Figure 5 | Effect of biosorbent dose on metal uptake and percentage removal (pH: 2.6; contact time: 150 min; agitation speed: 200 rpm; temperature:  $30 \pm 2$  °C ( $303 \pm 2$  K)).

decreases from 0.25 to 0.05 for 50 mg L<sup>-1</sup> initial Pb ion concentration with increasing biosorbent dose from 0.2 g L<sup>-1</sup> to 1.0 g L<sup>-1</sup>.

### Effect of solution pH

The acidity of the solution is one of the most important factors which affect biosorption of metal ions. The biosorption experiments were carried out at different solution pH 2, 2.6, 4, 5 and 6 to find out the effect of solution pH on Pb ion uptake by the biosorbent. The biosorbent dose of 1.0 g L<sup>-1</sup> was used with three initial Pb ion concentrations of 50, 100 and 150 mg L<sup>-1</sup>, and the temperature ( $303 \pm 2$  K), agitation speed of 200 rpm, and contact time of 150 min were kept fixed. It was observed that maximum uptake occurred at pH 4 for all the three different initial Pb concentrations of 50, 100 and 150 mg L<sup>-1</sup> (Figure 6). Lower metal uptake at lower pH value than pH 4 may be due to the acidic medium of the solution; the hydrogen ions were there to occupy the active sites of the biosorbent surface which cause repulsion between hydrogen ions and metal ions (Vilar *et al.* 2005). It is worthy to mention here that the equilibrium pH values were varied in a narrow range with the initial pH values (refer inset figure). Maximum separation of Pb ion was observed at an equilibrium pH (as well as

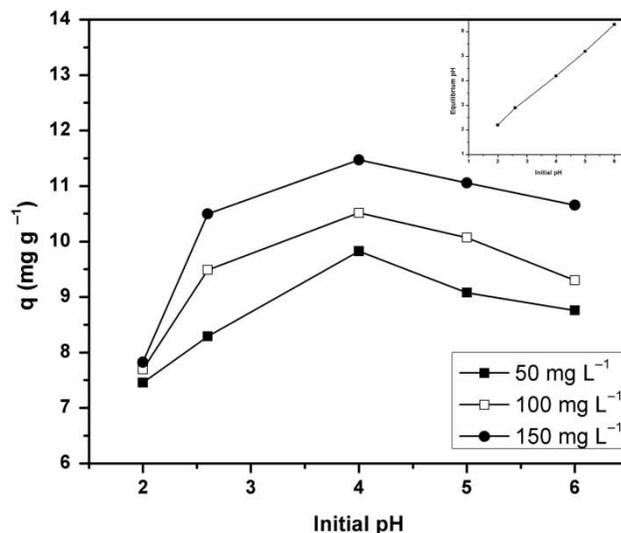


Figure 6 | Effect of solution pH on metal uptake (biosorbent dose: 1.0 g L<sup>-1</sup>; contact time: 150 min; agitation speed: 200 rpm; temperature:  $30 \pm 2$  °C ( $303 \pm 2$  K)).

initial pH) of 4 as maximum active sites were available for sorption. An appreciable decrease in uptake was observed after pH 4, which continued until pH 6. Beyond pH 6, precipitate formation was observed in Pb solution and therefore the experiments were terminated at this pH level. The decrease in metal uptake after pH 4 may be due to formation of hydroxide of lead ion which indicates precipitation of

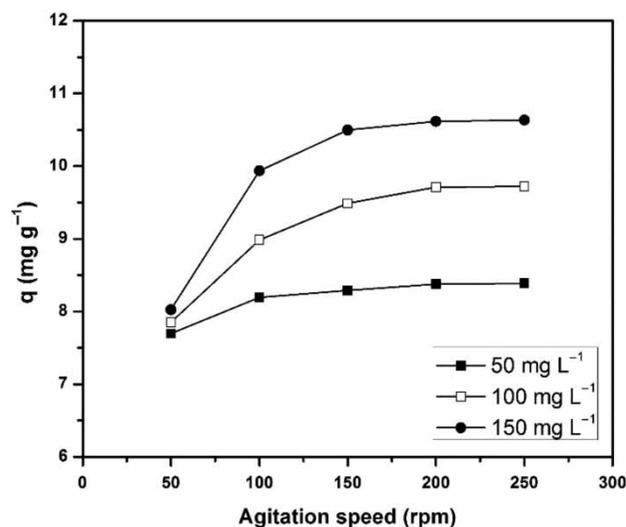
metal ions has been started at pH 5 (Gupta & Ali 2004; Vilar et al. 2005).

### Effect of agitation speed

Turbulence in the solution is necessary to overcome the mass transfer resistance offered by the thin liquid film surrounding the adsorbent particles. Biosorption experiments were performed to find out the effect of agitation speed on metal ion uptake, the solution containing Pb ion in concentrations of 50, 100 and 150 mg L<sup>-1</sup> with 1.0 g L<sup>-1</sup> of biosorbent were agitated at room temperature (303 ± 2 K) using incubator shaker at different rotational speed viz. 50, 100, 150, 200 and 250 rpm. The results are plotted as agitation speed (rpm) vs. metal uptake  $q$  (mg g<sup>-1</sup>) in Figure 7, which shows that the Pb ion uptake was increased with the increase in agitation speed. The increase in metal uptake was observed from 50 to 200 rpm agitation speed and after that it almost approached a constant. The results indicate that the agitation speed of 200 rpm was sufficient to create such turbulence in solution, which allows Pb ions to overcome the mass transfer resistance offered by thin liquid film surrounding the adsorbent particle and make available all the surface binding sites of the adsorbent for Pb uptake.

### Effect of temperature

The biosorption capacity of parthenium (*P. hysterophorus* L.) at different temperatures was tested at 20, 30, 40 and 50 °C



**Figure 7** | Effect of agitation speed on metal uptake (pH: 2.6; biosorbent dose: 1.0 g L<sup>-1</sup>; contact time: 150 min; temperature: 30 ± 2 °C (303 ± 2 K)).

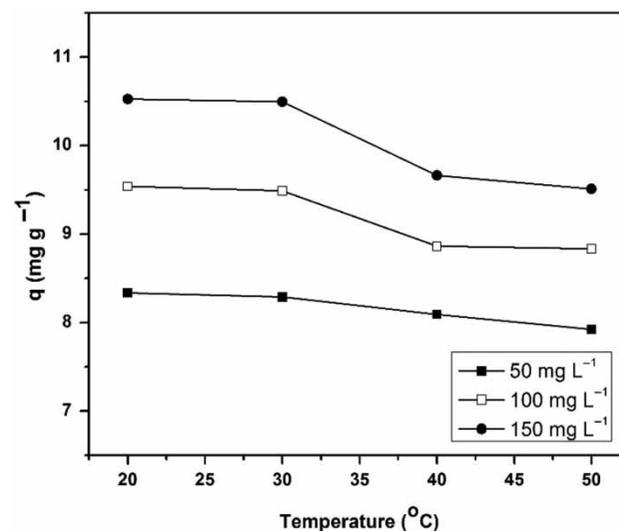
(293, 303, 313 and 323 K) for three different initial Pb ion concentrations of 50, 100 and 150 mg L<sup>-1</sup>. The experiments were performed using agitation speed of 200 rpm and natural solution pH for equilibrium contact time of 150 min using biosorbent dose of 1.0 g L<sup>-1</sup>. The effect of temperature on metal uptake is shown in Figure 8; it can be seen that maximum metal uptake was 8.34, 9.54 and 10.53 mg g<sup>-1</sup> for parthenium (*P. hysterophorus* L.) happening at 20 °C (293 K) for initial Pb ion concentrations of 50, 100 and 150 mg L<sup>-1</sup>, respectively. However, the increase in temperature was not affecting much on the metal uptake. Decreases in metal uptake with increasing temperature indicate that the biosorption process was exothermic in nature.

### Adsorption kinetics

The adsorption kinetics of Pb ion biosorption on parthenium (*P. hysterophorus* L.) were tested using pseudo-first-order model given by Lagergren Equation (3) (Lagergren 1898), pseudo-second-order model Equation (4) (Ho & McKay 2000) and Weber–Morris model Equation (5) (Weber & Morris 1963). The pseudo-first-order Lagergren model is expressed as:

$$\log(q_e - q) = \log q_e - \left(\frac{K'}{2.303}\right) t. \quad (3)$$

where  $q_e$  and  $q$  are the mass of metal adsorbed (mg g<sup>-1</sup>) at equilibrium and time  $t$  (min),  $K'$  is the first-order reaction rate constant of biosorption (min<sup>-1</sup>).



**Figure 8** | Effect of temperature on metal uptake (pH: 2.6; biosorbent dose: 1.0 g L<sup>-1</sup>; contact time: 150 min; agitation speed: 200 rpm; temperature: 20, 30, 40 and 50 °C (293, 303, 313 and 323 K)).

Pseudo-second-order equation is expressed as:

$$\frac{t}{q} = \left[ \frac{1}{K''q_e^2} \right] + \frac{t}{q_e} \quad (4)$$

where  $q_e$  and  $q$  are the mass of metal adsorbed ( $\text{mg g}^{-1}$ ) at equilibrium and time  $t$  (min) and  $K''$  is the pseudo-second-order rate constant of biosorption ( $\text{mg g}^{-1} \text{min}^{-1}$ ).

The intra-particle diffusion was determined by using the equation described by Weber–Morris, expressed as:

$$K_p = \frac{q}{t^{0.5}} \quad (5)$$

where  $q$  ( $\text{mg g}^{-1}$ ) is the amount adsorbed at time  $t$  (min) and  $K_p$  is the intra-particle rate constant ( $\text{mg g}^{-1} \text{min}^{-1/2}$ ).

To calculate kinetic models rate constants, the pseudo-first-order Lagergren Equation (3), the pseudo-second-order Equation (4) as well as the Weber–Morris Equation (5) were fitted with biosorption equilibrium data. The value of all kinetic models rate constants, correlation coefficients with the sum of the squared errors are tabulated in Table 1. Figures 9–11 show biosorption equilibrium data fitting with first-order Lagergren kinetic model, pseudo-second-order kinetic model, and Weber–Morris model, respectively. Comparing the pseudo-first-order kinetic model (Figure 9) and the pseudo-second-order kinetic model (Figure 10), the rate constants suggest that biosorption equilibrium data of Pb by parthenium (*P. hysterophorus* L.) fitted well with the pseudo-second-order kinetic model rather than the pseudo-first-order kinetic model. Further, it was evident from the values of  $q_e$  obtained by the pseudo-second-order kinetic model was close to the experimental  $q_e$  value (Table 1), whereas that of pseudo-first-order  $q_e$  value did not agree with the

experimental value. The equilibrium biosorption data of parthenium (*P. hysterophorus* L.) and Weber–Morris kinetics model fitting revealed the nonlinear relationship behavior between metal uptake and time for entire time range (Figure 11). This trend indicates that more than one process was affecting the biosorption process. Among all tested kinetics models, the biosorption of Pb ion by parthenium (*P. hysterophorus* L.) was best described by the pseudo-second-order kinetic model ( $R^2 = 0.99$ ).

## Adsorption isotherms

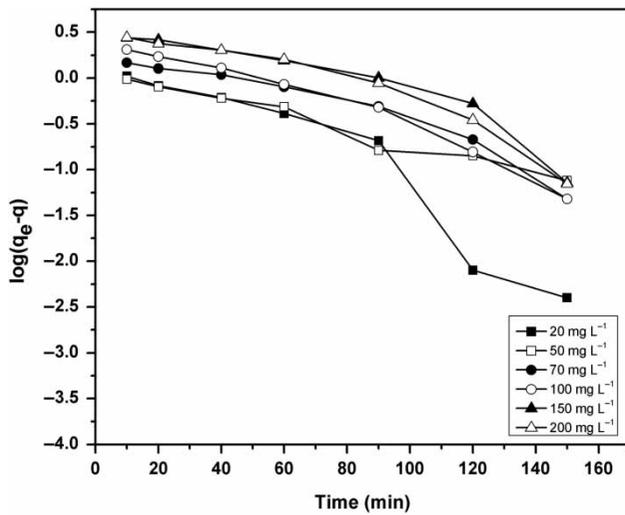
Various isotherms models are widely employed to understand the adsorption equilibrium behavior of the system and to model the equilibrium sorption system. The equilibrium data of Pb ion biosorption on parthenium (*P. hysterophorus* L.) were analyzed using Langmuir isotherm model (Langmuir 1916), Freundlich isotherm model (Freundlich 1906) and D-R isotherm model (Hobson 1969). The isotherm constants, correlation coefficient ( $R^2$ ) of these models for sorption of Pb onto parthenium (*P. hysterophorus* L.) is presented in Table 2. Langmuir model is the simplest model capable of representing such behavior with some assumptions that if the adsorption occurs on a homogeneous surface by monolayer adsorption, there is no interaction between adsorbed ions and the energy is same for all active sites of adsorption (Langmuir 1916). The nonlinear form of Langmuir equation is represented as Equation (6):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (6)$$

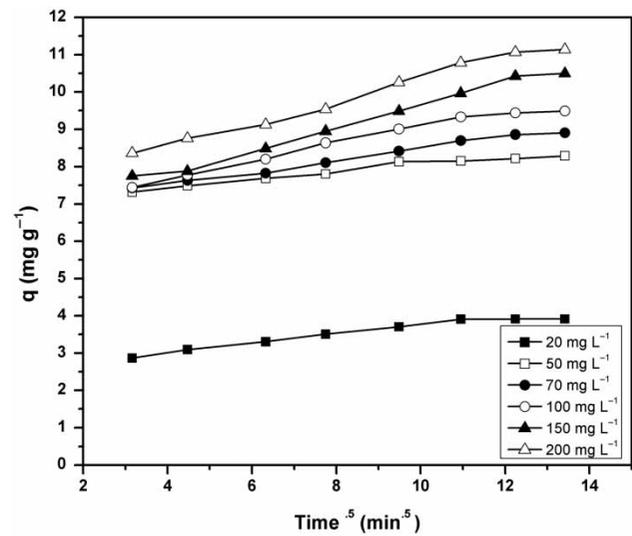
where  $q_e$  is the equilibrium metal ion concentration on the biosorbent ( $\text{mg g}^{-1}$ ),  $q_m$  is monolayer biosorption capacity

**Table 1** | Pseudo-first-order, pseudo-second-order and Weber–Morris kinetic model rate constants

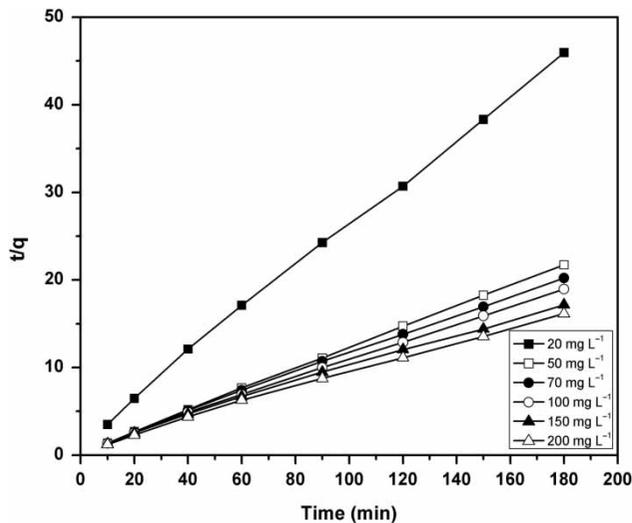
| Pb conc. ( $\text{mg L}^{-1}$ ) | Lagergren model                       |                              |                            |       |                             | Pseudo-second-order model    |  |       |                             | Weber–Morris model           |  |       |                             |
|---------------------------------|---------------------------------------|------------------------------|----------------------------|-------|-----------------------------|------------------------------|--|-------|-----------------------------|------------------------------|--|-------|-----------------------------|
|                                 | Exp. $q_{max}$ ( $\text{mg g}^{-1}$ ) | $q_e$ ( $\text{mg g}^{-1}$ ) | $K'$ ( $\text{min}^{-1}$ ) | $R^2$ | $\sum(q_{exp} - q_{cal})^2$ | $q_e$ ( $\text{mg g}^{-1}$ ) | $K''$ ( $\text{mg g}^{-1} \text{min}^{-1}$ ) | $R^2$ | $\sum(q_{exp} - q_{cal})^2$ | $q_e$ ( $\text{mg g}^{-1}$ ) | $K_p$ ( $\text{mg g}^{-1} \text{min}^{-0.5}$ ) | $R^2$ | $\sum(q_{exp} - q_{cal})^2$ |
| 20                              | 3.92                                  | 1.54                         | 0.04                       | 0.887 | 0.5601                      | 4.07                         | 0.21   | 0.998 | 1.7318                      | 1.44                         | 0.11   | 0.949 | 0.0501                      |
| 50                              | 8.29                                  | 1.08                         | 0.02                       | 0.966 | 0.0313                      | 8.38                         | 0.01   | 0.999 | 0.0902                      | 1.30                         | 0.10   | 0.961 | 0.0313                      |
| 70                              | 8.90                                  | 1.47                         | 0.02                       | 0.903 | 0.1386                      | 9.09                         | 0.01   | 0.998 | 0.2970                      | 2.06                         | 0.15   | 0.987 | 0.0239                      |
| 100                             | 9.49                                  | 1.69                         | 0.03                       | 0.958 | 0.0756                      | 9.76                         | 0.01   | 0.999 | 0.1991                      | 2.83                         | 0.21   | 0.969 | 0.1141                      |
| 150                             | 10.50                                 | 1.99                         | 0.02                       | 0.841 | 0.2484                      | 10.89                        | 0.01   | 0.996 | 0.6781                      | 3.93                         | 0.29   | 0.989 | 0.0773                      |
| 200                             | 11.14                                 | 1.99                         | 0.02                       | 0.893 | 0.1779                      | 11.55                        | 0.01   | 0.997 | 0.4732                      | 3.91                         | 0.29   | 0.983 | 0.1174                      |



**Figure 9** | Pseudo-first-order Lagergren kinetic model for Pb ion adsorption on parthenium (*P. hysterophorus* L.).



**Figure 11** | Weber-Morris kinetic model for Pb ion adsorption on parthenium (*P. hysterophorus* L.).



**Figure 10** | Pseudo-second-order kinetic model for Pb ion adsorption on parthenium (*P. hysterophorus* L.).

of the biosorbent ( $\text{mg g}^{-1}$ ),  $C_e$  is the equilibrium metal ion concentration in the solution ( $\text{mg L}^{-1}$ ) and  $K_L$  is the Langmuir biosorption constant ( $\text{L mg}^{-1}$ ).

The Langmuir isotherm model for Pb ion sorption onto parthenium (*P. hysterophorus* L.) fitted better to the experimental equilibrium sorption data. The calculated value of monolayer biosorption capacity of the biosorbent ( $q_m$ ) by Langmuir isotherm model was  $11.23 \text{ mg g}^{-1}$  ( $R^2 = 0.99$ ) which is almost similar to experimentally obtained maximum uptake value.

Separation factor  $R_L$  is a dimensionless constant of Langmuir isotherm which indicates the feasibility of the

biosorption process (Ertugay & Bayhan 2008). Separation factor  $R_L$  can be explained by Equation (7):

$$R_L = \frac{1}{1 + K_L C_o} \quad (7)$$

where  $C_o$  ( $\text{mg L}^{-1}$ ) is the initial concentration of Pb ion. The value of separation factor  $R_L$  gives an idea about the feasibility of adsorption process whether adsorption is favorable, unfavorable, linear or irreversible. The magnitude of  $R_L$  is a positive number which determines the feasibility of adsorption process. The value of  $R_L$  as 0.19 indicates favorable biosorption of Pb ion onto parthenium (*P. hysterophorus* L.) (Ertugay & Bayhan 2008). The parameters and constants of Langmuir isotherm model are listed in Table 2.

The Freundlich isotherm model is empirical in nature which assumes the adsorption takes place on a heterogeneous surface by multilayer adsorption. The further this model assumes, the stronger binding sites are occupied first and that the binding strength decreases with increasing degree of site occupation. It also assumes that the amount of adsorbate adsorbed increases infinitely with an increase in concentration (Freundlich 1906). The nonlinear relation of Freundlich isotherm model can be expressed as Equation (8):

$$q_e = K_F C_e^{1/n} \quad (8)$$

where  $q_e$  is the equilibrium metal ion concentration on the biosorbent ( $\text{mg g}^{-1}$ ),  $C_e$  is the equilibrium metal ion

concentration in the solution ( $\text{mg L}^{-1}$ ),  $K_F$  is Freundlich model constants related to the adsorption capacity and  $1/n$  is Freundlich model constants related to the intensity of adsorption. The values of  $K_F$  and  $1/n$  of the biosorbent are tabulated in Table 2. The calculated  $1/n$  value for this system is between 0 and 1, indicating that the biosorption of Pb ion onto the biosorbent parthenium (*P. hysterophorus* L.) is favorable at studied conditions.

The adsorption data were also examined to D-R model (Hobson 1969). The D-R model is represented as Equation (9):

$$q_e = q_m \exp(-Be^2) \quad (9)$$

$$e = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (10)$$

$$E = \frac{1}{\sqrt{2B}} \quad (11)$$

where  $q_m$  is the theoretical saturation capacity ( $\text{mg g}^{-1}$ ),  $B$  is a constant related to adsorption energy ( $\text{mol}^2 \text{kJ}^{-2}$ ),  $e$  is the Polanyi potential can be calculated by using Equation (10),  $R$  is the gas constant ( $\text{kJ mol}^{-1} \text{K}^{-1}$ ), and  $T$  is the temperature (K). The constant  $B$  is related to the energy of adsorption ( $E$ ,  $\text{kJ mol}^{-1}$ ) per molecule of adsorbate, was calculated by using Equation (11).

The value of mean free energy of biosorption gives an idea about biosorption mechanism, whether the biosorption that occurred is physical or chemical (Srividya & Mohanty 2009). The value of  $E$  between 8 to  $16 \text{ kJ mol}^{-1}$  signifies that the biosorption process takes place chemically, and the value of  $E$  less than  $8 \text{ kJ mol}^{-1}$  signifies that the biosorption process takes place physically. In the present study, the value of  $E$  calculated is  $12.03 \text{ kJ mol}^{-1}$ , which suggests that chemical ion exchange mechanism could have taken a significant role in biosorption process. However, the

correlation coefficients for the D-R isotherm model were found to be lower than that of Freundlich model.

### Analysis of the thermodynamic parameters

The thermodynamics variables such as Gibbs free energy ( $G$ ), enthalpy ( $H$ ), and entropy ( $S$ ) are the important parameter to describe the thermodynamic behavior of the biosorption process. These parameters can be written in terms of temperature and concentration as Equations (12) and (13):

$$\Delta G = -RT \ln K_d \quad (12)$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (13)$$

where  $R$  is universal gas constant ( $8.314 \text{ J mol}^{-1} \text{K}^{-1}$ ),  $T$  is temperature (K), and  $K_d$  is distribution coefficient which was calculated by using Equation (14):

$$K_d = \frac{C_a}{C_e} \quad (14)$$

where  $C_a$  is the concentration of Pb ion adsorbed on parthenium (*P. hysterophorus* L.), and  $C_e$  is the concentration of Pb ion in solution at equilibrium (Aravindhana et al. 2007).

The values of distribution coefficient ( $K_d$ ) were calculated for  $50 \text{ mg L}^{-1}$  of initial Pb ion concentration in solution at different temperatures, and corresponding values of  $\Delta G$  were computed using Equation (12). The negative value of the change in Gibbs free energy ( $\Delta G$ ) signifies that the Pb ion sorption onto parthenium (*P. hysterophorus* L.) was a feasible and spontaneous process at studied conditions (Table 3). However, the decreasing trend of  $\Delta G$  value with increasing temperature was observed which indicates that feasibility of the process decreases with increasing

Table 2 | Isotherms parameters for biosorbent

| Langmuir isotherm model          |        | Freundlich isotherm model   |        | D-R isotherm model                    |        |
|----------------------------------|--------|-----------------------------|--------|---------------------------------------|--------|
| Parameters                       | values | Parameters                  | values | Parameters                            | values |
| $q_{max}$ ( $\text{mg g}^{-1}$ ) | 11.23  | $k$                         | 4.91   | $q_{max}$ ( $\text{mg g}^{-1}$ )      | 27.63  |
| $K_L$ ( $\text{L mg}^{-1}$ )     | 0.21   | $1/n$                       | 0.17   | $B$ ( $\text{mol}^2 \text{kJ}^{-2}$ ) | 0.0034 |
| $R_L$                            | 0.19   | -                           | -      | $E$ ( $\text{kJ mol}^{-1}$ )          | 12.04  |
| $R^2$                            | 0.995  | $R^2$                       | 0.941  | $R^2$                                 | 0.942  |
| $\sum(q_{exp} - q_{cal})^2$      | 0.5029 | $\sum(q_{exp} - q_{cal})^2$ | 1.5562 | $\sum(q_{exp} - q_{cal})^2$           | 0.0335 |

**Table 3** | Thermodynamics parameters of biosorption process calculated for 50 mg L<sup>-1</sup> of initial Pb ion concentration

| T (K) | ln K <sub>d</sub> | ΔG (kJ mol <sup>-1</sup> ) | ΔH (kJ mol <sup>-1</sup> ) | ΔS (J mol <sup>-1</sup> ) |
|-------|-------------------|----------------------------|----------------------------|---------------------------|
| 293   | 1.61              | -3.92                      |                            |                           |
| 303   | 1.53              | -3.85                      | -7.06                      | -10.64                    |
| 313   | 1.44              | -3.74                      |                            |                           |
| 323   | 1.34              | -3.60                      |                            |                           |

temperature. The values of change in enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) were calculated from the slope and intercept of  $\ln K_d$  vs  $1/T$  (Equation (13)) plot respectively. The estimated values of  $\Delta H$  and  $\Delta S$  were  $-7.06$  kJ mol<sup>-1</sup> and  $-10.64$  J mol<sup>-1</sup> respectively (Table 3). The negative value of  $\Delta H$  suggests that biosorption of Pb ion onto parthenium (*P. hysterophorus* L.) was an exothermic process. Also, the  $\Delta H$  value between 2.1 and 20.9 kJ mol<sup>-1</sup> suggested the biosorption of Pb ion on parthenium (*P. hysterophorus* L.) as a physical process. The negative value of the change in entropy ( $\Delta S$ ) is an indication of the decrease in the randomness at the solid/solution interface during the biosorption process.

### Comparison with other biosorbents

The Pb ion uptake capacity of various biosorbents reported in the literature along with the adsorbent parthenium (*P. hysterophorus* L.) used in this study is summarized in Table 4. From the present study, the maximum Pb ion uptake value  $q_m$  for parthenium (*P. hysterophorus* L.) was found to be 11.47 mg g<sup>-1</sup> for initial Pb ion concentration of 150 mg L<sup>-1</sup> at studied operating conditions. The

**Table 4** | Comparison of Pb ion uptake capacity of parthenium (*P. hysterophorus* L.) with other adsorbent found in the literatures

| Adsorbent                                | Uptake capacity (mg g <sup>-1</sup> ) | pH  | Reference               |
|--|---------------------------------------|-----|-------------------------|
| Fly ash                                  | 15.08                                 | 6.0 | Cho et al. (2005)       |
| Rice husk                                | 4.00                                  | 6.0 | Khalid et al. (1998)    |
| Oak stem                                 | 0.75                                  | 5.2 | Prasad & Freitas (2000) |
| Lichen ( <i>Cladonia furcata</i> )       | 12.30                                 | 5.0 | Sari et al. (2007)      |
| Hazel-nut shell                          | 1.78                                  | 4.0 | Cimino (2000)           |
| Parthenium ( <i>P. hysterophorus</i> L.) | 11.47                                 | 4.0 | Present study           |

maximum Pb ion uptake value by parthenium (*P. hysterophorus* L.) obtained in the present study is comparable with other biosorbent. The cost and practicability of the biosorption process mainly lie on the cost, availability, and sustainability of biosorbent. The biosorbent used in the present study is abundantly available free of cost, widely spread, and itself is an environmental threat having no commercial applications. Also, by adding the labor charge for raw adsorbent collection, drying and grinding, storage and transportation, the overall cost for biosorbent preparation is very low as compared to expensive adsorbent and resins. The biosorption results and this comparison indicate that parthenium (*P. hysterophorus* L.) appears to be an economical, sustainable and efficient biosorbent for Pb ion sorption from wastewater. Hence, parthenium (*P. hysterophorus* L.) as biosorbent for Pb ion biosorption could be a fruitful utilization of this hazardous weed.

### CONCLUSION

In this study, a low-cost, sustainable biosorbent was prepared from waste biomass of hazardous parthenium (*P. hysterophorus* L.) weed and used it in biosorption process for the treatment of Pb ion contaminated wastewater. The functional groups present in biomass were identified by FTIR transmittance spectra analysis and found that C-X, C-N, C=O, and C-O-C group were the main responsible functional groups for Pb ion sorption. The percentage removal of Pb ion was 98.3% achieved for initial Pb ion concentration of 50 mg L<sup>-1</sup> at the operating condition of biosorbent dose as 1.0 g L<sup>-1</sup>, pH 4, room temperature (303 ± 2 K), agitation speed as 200 rpm, and equilibrium contact time of 150 min. Also, it was observed that biosorption process was efficient when metal to the biosorbent ratio in solution was small (<0.05). The biosorption rate kinetics closely followed the pseudo-second-order kinetic model ( $R^2 = 0.99$ ). The adsorption isotherm of Pb ion adsorption on parthenium (*P. hysterophorus* L.) weed was best described by Langmuir isotherm model ( $R^2 = 0.99$ ) which suggest monolayer adsorption of Pb ion on the adsorbent. The calculated thermodynamic parameters indicate that biosorption process was a feasible, spontaneous process and exothermic in nature. The biosorption results suggested that parthenium (*P. hysterophorus* L.) weed is an efficient, low-cost and sustainable biosorbent for the removal of Pb ion from aqueous solutions.

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