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Green mediated biosorption of Pb(II) from aqueous solution using chemically modified low-cost *Grewia optiva* leaves

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ABSTRACT

In this study, the green mediated biosorption of Pb(II) onto chemically modified *Grewia optiva* leaves (CMGOL) has been investigated. To improve the biosorption capacity, *Grewia optiva* leaves powder were treated with HNO_3, then neutralized and finally activated with $CaCl_2$. The prepared adsorbent was characterized by analytical tools such as Fourier-transform infrared spectroscopy, scanning electron microscopy, and Brunauer–Emmett–Teller surface area analyzer. To determine the optimum parameters of the biosorption process, batch experiments were performed under different conditions of pH (2–7), contact time (5–180 min), biosorbent dosage (0.1–30 g/L), initial metal concentration (10–800 mg/L), and temperature (25°C–50°C). Optimal biosorption of Pb was achieved at pH 6, biosorbent dosage 5 g/L, contact time 120 min, initial Pb concentration 100 mg/L, and temperature of 50°C. Correlation coefficient R^2 value (0.967) of Langmuir adsorption model (monolayer adsorption capacity = 135.136 mg/g) was high as compared to the Freundlich adsorption model and thus fitted well the equilibrium adsorption data. Kinetic studies revealed that Pb biosorption data fitted well to the pseudo-second-order equation rather than the pseudo-first-order equation. The values of thermodynamic parameters $\Delta H°$ and $\Delta G°$ were negative while that of $\Delta S°$ was positive indicating favorable and spontaneous nature of the biosorption process. Due to high biosorption capacity (135.136 mg/g) the prepared CMGOL could be used effectively for the removal of Pb from wastewaters.

Keywords: Grewia optiva leaves; Biosorbent; Lead; Wastewaters

1. Introduction

Heavy metals are important from an industrial point of view as they are used in making vehicles, weapons, parts of different instruments, airplanes, etc. They have a significant role in normal body functioning as well. About 1/3rd of all enzymatic reactions need metal ions as an activator in some cases while in other cases they are an integral part of

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enzyme structures. However, if taken in the excess amount they would cause a number of health complications which in severe cases could lead to death. The primary route of entry into the human body is the prevalent contamination of water bodies with heavy metals. Due to their technological importance in the development of a country their use cannot be abandoned. Consequently, new methods are being sought to properly stop their entries into water bodies [1]. According to the US Environmental Protection Agency, Pb is a toxic metal [2] which is non-biodegradable. Its bioaccumulation in living tissues causes health complications. Excess amount of lead in drinking water (above safe level = 5 ng/mL) may trigger numerous diseases in humans like nephritic syndrome, anemia, and hepatitis. Additionally, lead toxicity also causes kidney, nervous, and reproductive systems disorder [3–5]. The main sources of lead contamination of water bodies are lead storage batteries production, oil refineries, smelting, mining, and paint industries [6–8].

For the removal of lead from industrial effluents various physicochemical methods like adsorption, chemical precipitation, ions exchange, electrolytic recovery, electrodialysis, reverse osmosis, ozonation, solvent extraction, membrane separation, foam filtration, ultra-filtration, vapor recovery, photochemical methods, freeze crystallization, and gamma irradiation is being in use [9,10]. Financial consideration and operational complications associated with the mentioned approaches effect their practicabilities in the field. Also the physicochemical methods are associated with a large amount of sludge formation. A special type of adsorption; the biosorption is a process where agricultural wastes or natural products are used as a raw material in the production of an adsorbent (biosorbent) [11–13]. The cell wall of *Grewia optiva* leaves contains functional groups like hydroxyl, amino, carboxyl, etc. [14–16] which could be helpful in binding the heavy metals if used as biosorbent.

Grewia optiva is planted on roadsides for soil conservation and their leaves are abundantly available as waste biomass. To best of our knowledge *Grewia optiva* leaves have not been used as biosorbent for the removal of toxic metals like lead by any researcher. Therefore, the present study was aimed to use *Grewia optiva* leaves as a cost-effective and efficient biosorbent for the removal of Pb from water.

2. Materials and methods

2.1. Biosorbent preparation and modification

The leaves of *Grewia optiva* were collected from Bajaur Agency, Pakistan. They were initially rinsed with tap water and then twice with deionized water to eliminate dust particles and soluble impurities. Then they were kept in shade till dryness. The dried leaves were then kept in an electrical oven at 40°C for 24 h to eliminate moisture content. The leaves were then ground using an electric grinder and sieved to 44 mesh size (Fig. 1). About 100 g of the powdered sample was wetted in 2 L, HNO_3 (Sigma-Aldrich, Germany) solution (0.1 M) for 24 h, followed by filtration through 41 Whatman Filter Paper and subsequently rinsed several times with deionized water. For neutralization 0.1 M, NaOH (Sigma-Aldrich, Germany) was used. The neutralized biosorbent was dried at room temperature and then in an electrical oven at 100°C. About 50 g of it was then subjected to activation with $CaCl_2$ solution (0.1 M) in 1 L. After activation the biosorbent was dried in the oven. The HNO_3 treatment was applied to remove the previously bounded metals to the raw material while $CaCl_2$ (Sigma-Aldrich, Germany) treatment for the incorporation of a specific group to biosorbent that would be helpful in facilitating Pb ion exchange between solution and biosorbent.

2.2. Characterization of biosorbent

The Barrett–Joyner–Halenda (BJH), Brunauer–Emmett–Teller (BET) surface area, pore diameter, and pore volume were investigated by employing surface area analyzer (Quantachrome, USA, NOVAS200e). To understand the mechanism involved in biosorption or other words functional groups involved in lead binding, Fourier-transform infrared spectroscopy (FTIR) (PerkinElmer, USA) spectrum of chemically modified *Grewia optiva* leaves (CMGOL) before and after biosorption, was drawn in the frequency range of 400–4,000 cm^{-1}. Scanning electron microscopy (SEM) analysis was performed to view clear differences between the treated and untreated *Grewia optiva* leaves.

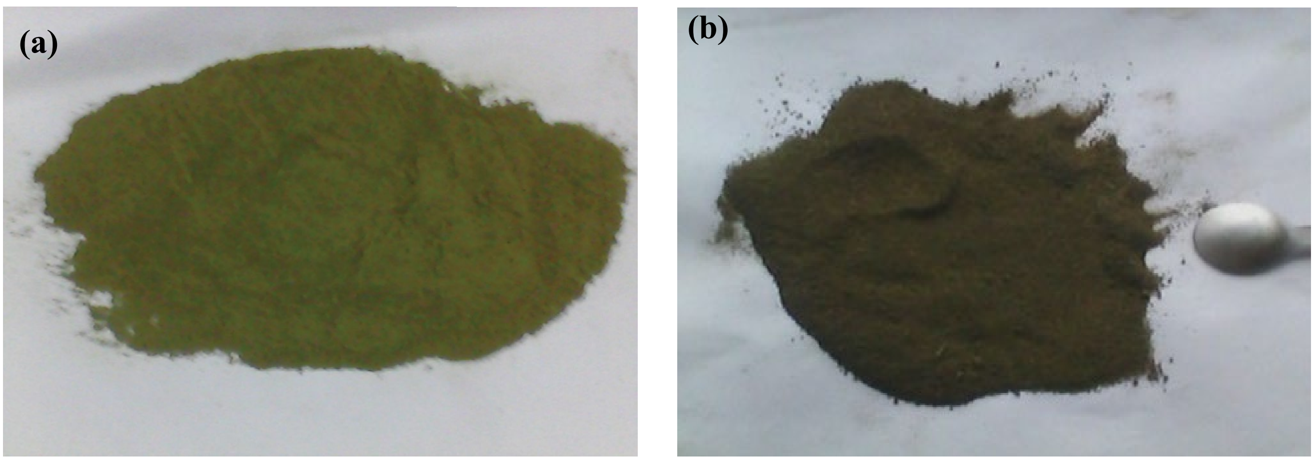

Fig. 1. (a) Untreated GOL and (b) GOL after treatment.

2.3. Adsorption experiments

The stock solution of $Pb(NO_3)_2$ (Sigma-Aldrich, Germany) was prepared by dissolving 1,000 mg of it in 1 L distilled water, which was further diluted with deionized water to obtain working standards (100 to 800 mg/L). In batch investigation 100 mL of $Pb(NO_3)_2$ working standards were contacted 0.5 g of biomass and shaken at a speed of 130 rpm for 2 h. The solutions were then filtered with Whatman Filter Paper. The filtrate was subjected to atomic absorption spectrophotometer analysis for Pb(II) ion concentration. The biosorption capacity q_e (mg/g) and % uptake of Pb were calculated using Eqs. (1) and (2).

$$q_e = \left(C_i - C_f\right) \times \frac{v}{m} \tag{1}$$

$$\%R = \frac{\left(C_i - C_f\right)}{C_i} \times 100 \tag{2}$$

where C_i denotes metal initial concentration and C_f, represents the final metal concentration, V is the volume of test solution in L and m is the mass of biosorbent in grams.

2.4. Isotherm study

The Pb(II) biosorption on CMGOL was studied by varying initial metal concentration in the range of 20–800 mg/L. Other parameters like pH of the solution (6), solution volume (100 mL), contact time (120 min), and biosorbent mass (5 g/L) were kept constant. Their q_e values were calculated from equation (1) and plotted against concentration. Freundlich and Langmuir's models were applied to analyze the biosorption equilibrium data.

2.5. Adsorption kinetics

To determine kinetic parameters of Pb(II) biosorption on CMGOL, a fixed quantity of biosorbent (0.5 g) was added to 100 mL of Pb(II) solution (100 mg/L). The solutions were shaken for 120 min at 130 rpm. Pseudo-first-order and pseudo-second-order models were applied to explain the kinetics of biosorption.

2.6. Effect of pH and biosorbent mass

Effect of pH on Pb(II) biosorption on CMGOL was studied in the pH range of 2–7. The solution pH was adjusted using HNO_3 (0.1 M) and NaOH (0.1 M). The effect of biosorbent mass was investigated from 0.1–30 g/L. All other parameters were kept constant.

2.7. Determination of thermodynamic parameters

The effect of temperature on Pb(II) biosorption onto CMGOL was analyzed at 25°C, 30°C, 40°C, and 50°C, keeping all other parameters constant.

3. Results and discussion

3.1. Characterization of prepared biosorbent

3.1.1. FTIR spectra before and after loading Pb(II)

The possible interactions between the metal ion and functional group present on biosorbent were studied using FTIR spectroscopy. The spectra of CMGOL and Pb loaded CMGOL have been shown in Figs. 2a and b, respectively. In Fig. 2a the peak at 3,352 cm^{-1} represents the hydroxyl group while the peak at 2,926 cm^{-1} represents a C–H bond. The peak at 2,854 cm^{-1} shows an aldehyde group. The C=C bond stretches observed at 1,614 cm^{-1} representing alkenes and aromatic compounds in CMGOL. FTIR image of Pb(II) loaded CMGOL reflect shifting of peak from 3,352 to 3,346 cm^{-1} and 2,926 to 2,924 cm^{-1}. The peak shifting indicates some sort of interaction between the metal ion and OH, C–H, and C=C groups.

3.1.2. Surface area, pore diameter, and volume

The surface area and other related parameters of CMGOL and untreated biomass are given in Table 1. The recorded data explain that CMGOL has a greater surface area with improved porosity which renders it a capable biosorbent having high biosorption capacity as compared to untreated

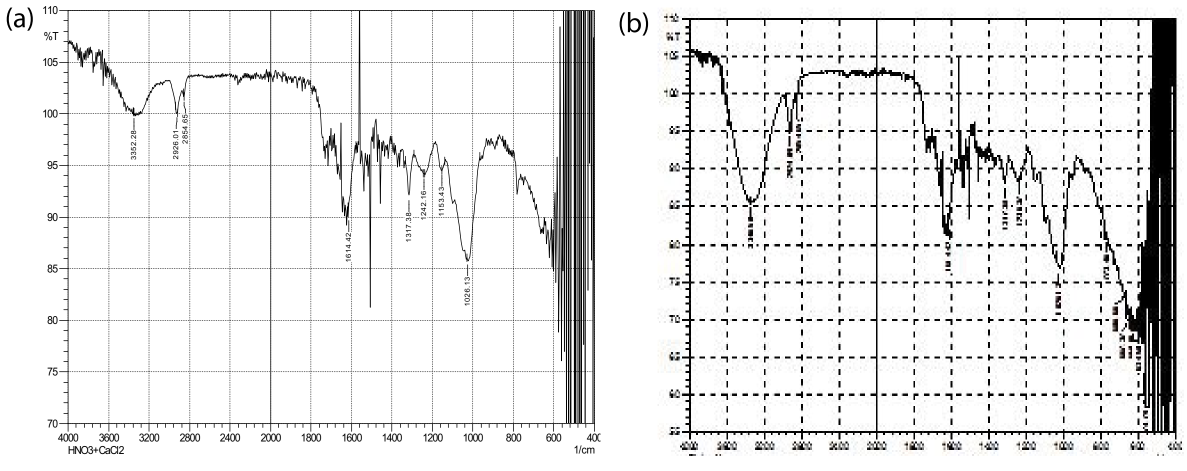

Fig. 2. FTIR spectra of (a) unloaded CMGOL and (b) Pb(II) loaded CMGOL.

biomass. Table 1 shows the BET and BJH surface area, pore diameter, and pore volume of prepared biosorbent.

3.1.3. SEM micrographs of treated and untreated biosorbent

SEM analysis of treated and untreated biomass was performed to observe texture and surface morphological differences between the two (Figs. 3a and b). The SEM photograph confirmed the treated biosorbent surface as multi porous in nature. Most of the pores are nearly round shaped in morphology with a pore diameter of about 5 µm. If we compare Figs. 3a and b, significant structural differences can be observed between the two. Well, uniform three-dimensional structures with adhered small particles can be seen (Fig. 3b) for treated biosorbent. The adhered small particles may probably be $CaCl_2$ particles that have been incorporated during activation.

Table 1
Surface area, pore diameter, and volume of CMGOL

Biosorbent	Untreated biomass	CMGOL
BET surface area (m^2/g)	45.76	285.73
BJH surface area (m^2/g)	13.64	70.05
Pore diameter (Å)	20.34	129.03
Pore volume (cc/g)	0.34	0.93

3.2. Effect of pH

The effect of pH on Pb biosorption was studied in the range of 2–7. The pH of solutions was adjusted using NaOH (0.1 M) and HNO_3 (0.1 M) solutions. Fig. 4 shows that the percent uptake of Pb(II) increases with a rise in pH up to pH 6. At lower pH, due to high hydrogen ion concentration the adsorption sites became positively charged which then repel the positively charged Pb ion and thus encounters little biosorption [17]. At lower pH (2–5) Pb exists as Pb(II) ion and at pH higher Pb combine with OH^- forming $Pb(OH)_2$ and $Pb(OH)^+$ [17]. Highest Pb(II) uptake was observed at pH 6. Therefore, all the biosorption experiments were performed at pH 6.

3.3. Effect of contact time

Fig. 5 presents the influence of contact time on the biosorption of lead by prepared biosorbent. The figure shows that the rate Pb biosorption by CMGOL up to 10 min was quite high which then became steady till to 120 min

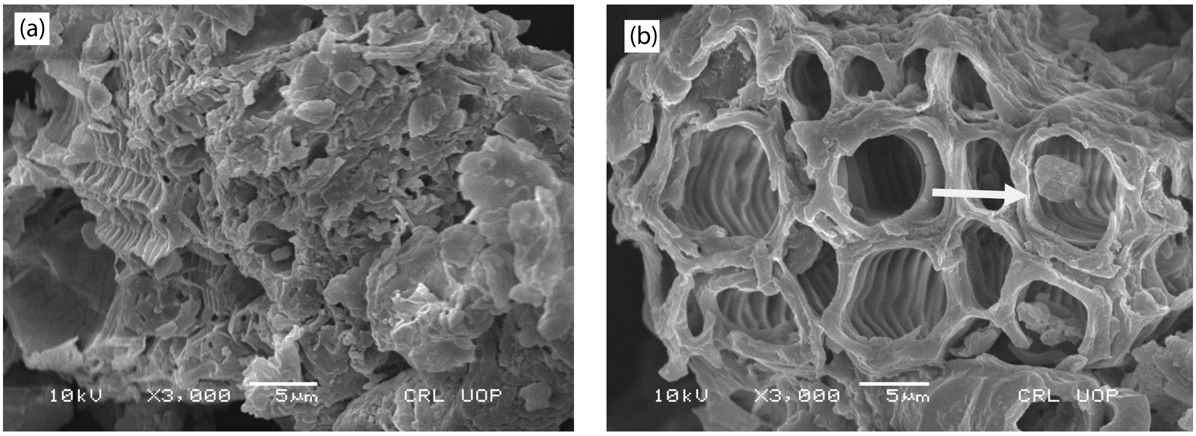

Fig. 3. SEM images of (a) un-treated biomass and (b) treated biomass.

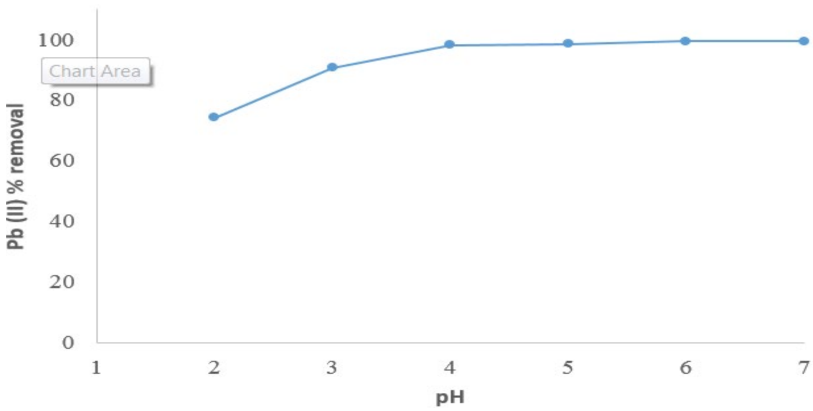

Fig. 4. Effect of pH on Pb(II) removal by CMGOL.

at which the maximum removal efficiency was observed. Thus 120 min contact time was noted as equilibrium biosorption time and in almost all experiments shaking were done for 120 min.

3.4. Effect of biosorbent mass

The effect of biomass dosage (1–30 g/L) on Pb(II) uptake is shown in Fig. 6. The percent removal of lead increased with an increase in biosorbent dosage from 1–5 g/L which then became steady. Thus 5 g/L adsorbent dose was used as an optimum dose in subsequent experiments. The decrease in percent removal at higher doses may be due to the aggregation of biomass that reduces the active surface area of biosorbent [18].

3.5. Effect of initial metal ion concentration

The available literature findings suggest that the removal potential of metal by a given adsorbent increases with an increase in initial metal concentration with in certain limits and beyond that limit there is no further increase in the uptake capacity as saturation of adsorbent occurs [18]. Fig. 7 shows the effect of initial lead ion concentration on its biosorption onto prepared biosorbent. Within the tested limit a linear correlation was observed between biosorption and Pb concentration.

3.6. Adsorption isotherm studies

Langmuir isotherm [19] in its linear form can be presented as follow:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} \times b} + \frac{C_e}{q_{\max}} \quad (3)$$

where q_e (mg/g) is the amount of metal biosorbed per unit mass of biosorbent at equilibrium. C_e (mg/L) represents equilibrium metal ion concentration, $q_{\max}$ is the monolayer adsorption capacity of biosorbent (mg/g). The term b is Langmuir constant related to free energy and binding strength. The plot of C_e vs C_e/q_e gives a straight line with $q_{\max}$ and b as slope and intercept respectively (Fig. 8). The R^2 value for this model was 0.967 (Table 2).

Freundlich adsorption isotherm [20] can be presented as follow:

$$\log q_{eq} = \log K_F + \left[\left(\frac{1}{n}\right)\left(\log C_{eq}\right)\right] \quad (4)$$

In Eq. (4), K_F is Freundlich constant and n is an empirical factor dealing with the strength of biosorption. Fig. 9 shows a plot of lnC_e verses lnq_e. For Freundlich adsorption isotherm the R^2 value was 0.8693. The value of "K_F" and "n" was obtained from the slope and the intercept of the given plot. Their values are given in Table 3.

Based upon correlation co-efficient R^2 values it was concluded that the best fit of the data could be obtained with the Langmuir adsorption isotherm rather than the Freundlich model.

3.7. Kinetic studies of biosorption

Adsorption kinetics is an important aspect of adsorption processes as it decides whether a given adsorbent would be effective in the removal of a given contaminant from wastewater or not. To estimate the kinetic parameters of Pb biosorption on prepared biosorbent, pseudo-first, and second-order models [21,22] were applied to the experimental data. Based on the regression constant values pseudo-second-order model fitted the kinetics data well. For the pseudo-first-order model the R^2 values were low (0.894). The pseudo-second-order equation in integrated form is expressed as in Eq. (5):

$$\frac{t}{q_t} = \frac{1}{K_2 \times q_e^2} + \frac{t}{q_e} \quad (5)$$

where K_2 (g/mg min) is the equilibrium rate constant of second-order kinetics model. The plot of t vs. t/q_t is shown in Fig. 10. Table 4 shows the values of different parameters like q_e, K_2, and R^2 of Pb biosorption. The value of R^2 was 0.999 which was quite high in comparison to the pseudo-first-order model. The values of q_e obtained from the pseudo-second-order kinetics model were in close agreement with

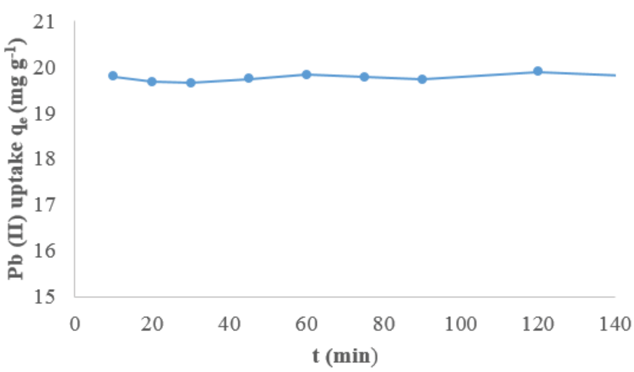

Fig. 5. Effect of contact time on Pb(II) removal by CMGOL.

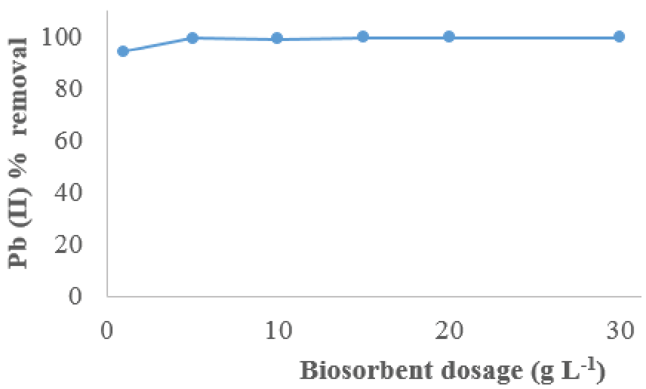

Fig. 6. Effect of biosorbent dosage on Pb(II) biosorption onto CMGOL.

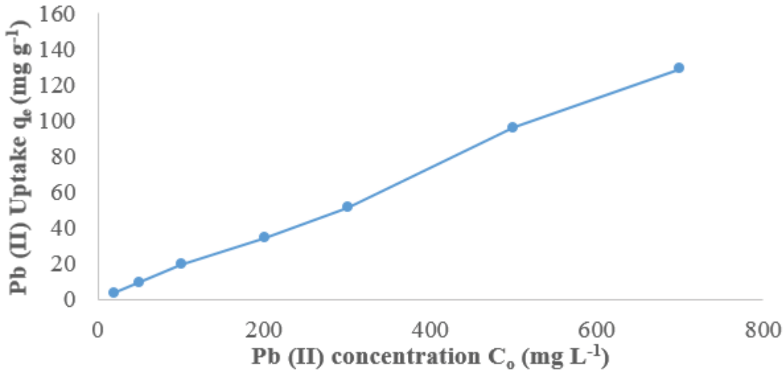

Fig. 7. Effect of Pb(II) ion concentration on biosorption.

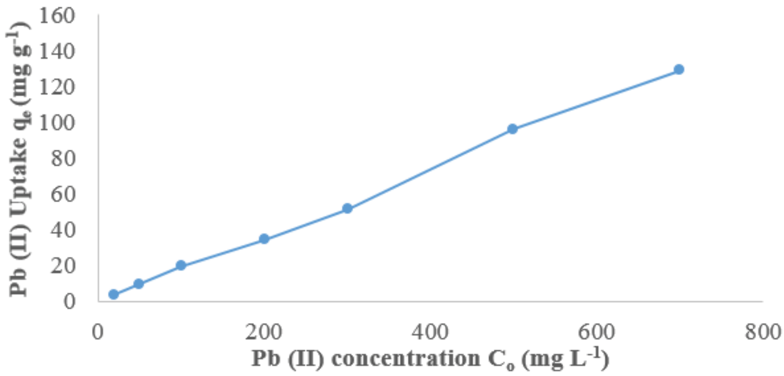

Fig. 8. Langmuir isotherm for Pb(II) removal onto CMGOL.

Table 2
Parameters of pseudo-second-order kinetics of Pb biosorption onto CMGOL

C_0 (mg/L)	100
Metal	Pb^{2+}
K_2 (g/mg min)	0.131
q_e (mg/g)	19.960
R^2	0.999

those obtained experimentally. Based on the R^2 values of the two models, it was concluded that the best fit of kinetics data could be obtained with a pseudo-second-order model (The graph of the pseudo-first-order model has not been shown in this paper).

3.8. Adsorption thermodynamics

Adsorption thermodynamics is crucial to investigate the nature (physical or chemical) and feasibility of the biosorption process. The knowledge of the endothermic or exothermic nature of a given process is very important from an industrial point of view. Enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) estimated Van't Hoff plot (Fig. 11).

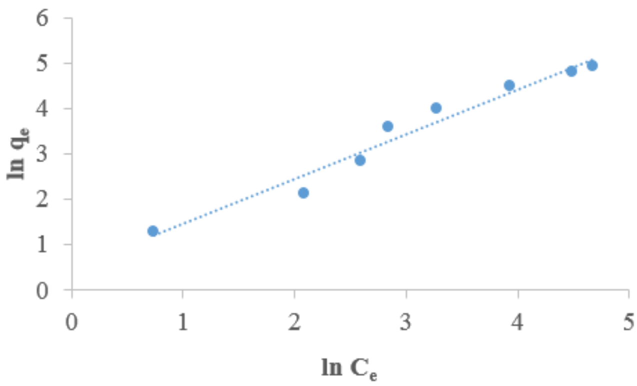

Fig. 9. Freundlich plot of Pb(II) biosorption onto CMGOL.

Van't Hoff equation can be presented as follows:

$$\ln K = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{6}$$

where $K = q_e/C_e$ represents the adsorption affinity while $\Delta H°$ and $\Delta S°$ represent the change in enthalpy and entropy respectively. The values of $\Delta H°$ and $\Delta S°$ were estimated from the slope and intercept of Van't Hoff plot and their values are given in Table 4.

Gibbs free energy change ($\Delta G°$) was calculated from Eq. (7) as given below:

$$\Delta G° = \Delta H° - T\left(\Delta S°\right) \quad (7)$$

The negative value of $\Delta H°$ suggests the exothermic nature of the biosorption process. The positive value of $\Delta S°$ indicating the favorable nature of biosorption. The negative value of $\Delta G°$ indicates the spontaneous nature and feasibility of the process.

Table 3
Langmuir and Freundlich constants for Pb(II) biosorption on CMGOL

Langmuir isotherm	
q_{max} (mg/g)	135.136
b (L/mg)	0.431
R^2	0.967
Freundlich isotherm	
K_F (mg/g)	17.7
$1/n$	2.26
R^2	0.869

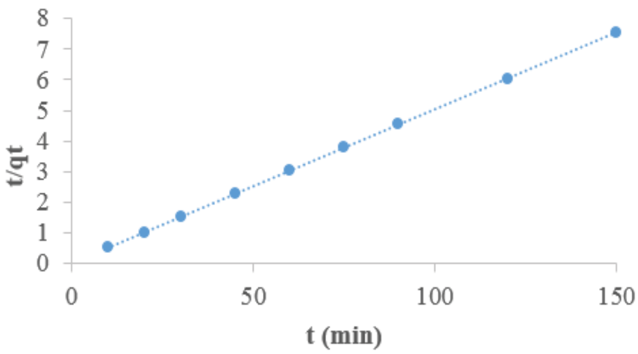

Fig. 10. Pseudo-second-order kinetic plot for Pb(II) removal onto CMGOL.

3.9. Comparison with other biomass-based adsorbents

A comparison made between the adsorption capacities of the prepared adsorbent and other biomass-based biosorbents is given in Table 5 [23–31]. It can be concluded from the results that our adsorbent has appreciable adsorption capacity that can be effectively used for the removal of heavy metals from water.

4. Conclusions

The applicability of *Grewia optiva* leaves as a biosorbent for Pb(II) removal was evaluated using a batch adsorption

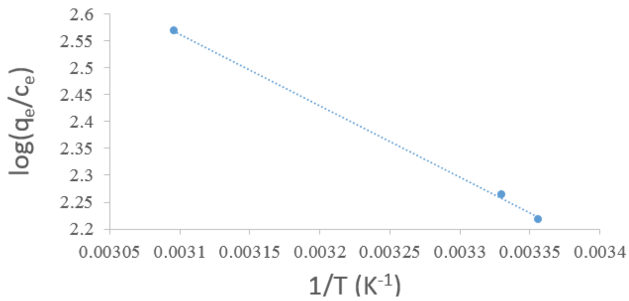

Fig. 11. The Van't Hoff's plot for the biosorption of Pb onto CMGOL.

Table 4
Thermodynamics parameter for biosorption of Pb(II) onto CMGOL

Biosorbent	CMGOL
$\Delta H°$ (J/mol K)	–25.509
$\Delta S°$ (J/mol K)	15.415
$\Delta G°$	
298 K	–4.568
303 K	–4.645
313 K	–4.799
323 K	–4.799

Table 5
Comparison of adsorption capacity of the present adsorbent with other biomass-based adsorbents

S. No.	Biosorbent	q_m (mg/g)	Reference
1	This research work	135.136	–
2	Green algae (*Spirogyra* sp.)	140	[23]
3	*Chlamydomonas reinhardtii*	96.3	[24]
4	Tea waste	65	[25]
5	Acid treated maize tassels	37.31	[26]
6	Nitric acid treated peanut shell activated carbon	35.5	[27]
7	Hazelnut shell	28.18	[28]
8	Apricot stone	22.85	[29]
9	*Pinus sylvestris*	22.22	[30]
10	*Phaseolus aureus* hulls	21.80	[31]

approach. The biosorbent was capable of Pb uptake from aqueous solution with biosorption capacity mainly dependent on initial pH, biosorbent dosage, contact time, initial metal concentration, and temperature. The optimum parameter identified through various experiments were pH = 6, biosorbent dose = 5 g/L, contact time = 120 min, initial Pb(II) concentration = 100 mg/L and temperature = 50°C. The biosorption equilibrium data obtained were fitted well by Langmuir isotherm rather than the Freundlich model with an R^2 value of 0.967. Kinetic study shows that Pb(II) biosorption follows pseudo-second-order kinetics rather than first order. The thermodynamic study revealed that Pb(II) biosorption on CMGOL was exothermic, favorable, and spontaneous in nature. Thus CMGOL which is low-cost green biosorbent and easily available could be effectively used for the removal of Pb(II) from wastewater.

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