Effective removal of Cd(II), Pb(II) and Cr(VI) from aqueous solution using *Bauhinia variegata* leaves after chemical modifications

Syed Muhammad Salman[a], Muhammad Zahoor[b,*], Aftab Majeed[a], Muhammad Wahab[a], Durr e Shahwar[c], Syed Nusrat Shah[d], Ezzat Khan[e]

[a]*Department of Chemistry, Islamia College University Peshawar, Peshawar, KPK, Pakistan,*
emails: salman@icp.edu.pk (S.M. Salman), aftabmajeed96@gmail.com (A. Majeed), mwahabbajaur@gmail.com (M. Wahab)
[b]*Department of Biochemistry, University of Malakand, Chakdara Dir Lower, KPK, Pakistan,*
email: mohammadzahoous@yahoo.com
[c]*Department of Zoology, Islamia College University Peshawar, Peshawar, KPK, Pakistan,*
email: salmanchemidst80@yahoo.com
[d]*Department of Chemistry, Bacha Khan University Charsadda, Charsada, Peshawar, KPK, Pakistan,*
email: syednusratshah1@gmail.com
[e]*Department of Chemistry, College of Science, University of Bahrain, Sakhir 32038, Bahrain,*
email: ezkhan@uob.edu.bh

ABSTRACT

This study deals with biosorption of Pb(II), Cd(II) and Cr(VI) from an aqueous solution using chemically modified *Bauhinia variegata* leaves (CMBVL); a low cost adsorbent under different experimental conditions likes initial heavy metals concentration (20–500 mg/L), contact time (10–120 min), pH (1–7), and biosorbent dose (1–30 g/L). The biosorption of the selected heavy metals follow Langmuir isotherm more effectively rather than the Freundlich model. The maximum biosorption capacity (q_{max}) of CMBVL for Pb(II), Cd(II) and Cr(VI) were; 92.592, 114.943, and 70.921 mg/g, respectively. Based on regression correlation coefficients (R^2) value the kinetic data were best fitted into second-order kinetic model rather than the first-order kinetic equation. The calculated thermodynamic parameters like standard enthalpy change ($\Delta H°$), standard entropy change ($\Delta S°$), and standard Gibb's free energy ($\Delta G°$) indicated that the biosorption of the selected metals was an exothermic, spontaneous, and favorable process. Based on our results, it can be concluded that CMBVL could be effectively extended as biosorbent for the removal of heavy metals from industrial effluents.

Keywords: Biosorption; Heavy metals; Langmuir and Freundlich isotherms

1. Introduction

Pollution of water sources due to the release of heavy metals in the aqueous effluents from industries causes severe environmental problem [1]. The adverse health impact of heavy metals like Pb(II), Cd(II) and Cr(VI) beyond their acceptable limits of 0.010, 0.005, and 0.05 mg/L, respectively, in drinking waters has already been established [2–4]. The presence of Pb(II) in a small amount in drinking water causes hepatitis, kidney, liver, nervous system, and reproductive system disorders [5]. Similarly, adverse health effects of Cd(II) include bone diseases, kidney disorders, cancer, skeletal deformation, Sciatica, and liver disorders [6,7]. The Cr(VI) is deadly toxic and causes

* Corresponding author.

cancer, ulceration, dermatitis, nervous system disorders, kidney, and liver diseases. Even it can cause death at higher concentrations [8]. Therefore, the removal of these toxic heavy metals from industrial effluents is very important to ensure human life on earth.

Various methods have been reported such as precipitation, reduction, electrolysis, solvent extraction, ion exchange, and membrane process to remove metal ions from aqueous solution [9]. Biosorption has been found to be a very simple, efficient, and effective method for the removal of heavy metal ions from wastewater as compared with other methods. However, due to the high cost of conventional adsorbents such as activated charcoal, there is a great interest in the use of low-cost, environment-friendly biosorbents [10]. Recently, agricultural wastes, food organic wastes, algae, fungi, bacteria, etc., as biosorbents for the removal of toxic heavy metals such as Pb(II), Hg(II), As(III/V), Cd(II), etc., or essential less toxic metals like Cu(II), Zn(II), Co(II), Ni(II), etc., from wastewater have been studied [11–17]. The sorption properties of biological wastes are due to high surface area and porosity associated with them [18].

Formerly, we have used chemically modified leaves of *Grewia optiva* for the removal of lead from its aqueous solution [19]. However, different biomasses have different phytochemical compositions and functional groups, and therefore, have different ability of attaching a particular metals ion. In the current research, a work biosorbent was prepared from locally available *Bauhinia variegata* plant leaves, chemically modified by $HNO_3/CaCl_2$, and was used to remove Pb(II), Cd(II) and Cr(VI) from aqueous solution. As biosorbent, the leaves of this plant has not been used before. The effect of experimental factors like heavy metals concentration, contact time, pH of solution, and biosorbent dosage were also studied.

2. Experimental

2.1. Collection of biomass and preparation of biosorbent

The leaves of *B. variegata* plant were collected from District Charsadda, KPK, Pakistan. Initially, the leaves were rinsed with tap water and then twice with double distilled water to remove dust particles and soluble impurities. The leaves were stored in shade for drying/dehydration for 2 weeks. The leaves were further placed in an electric oven at 46°C for 24 h. The crispy leaves were grinded into fine powder by an electrical grinder and were sieved to attain 44 mesh size powders. The mesh size powder was stored in an airtight bottle for further research work.

About 100 g leaves powder of *B. variegata* were mixed with 2 L of HNO_3 solution (0.1 M) and left over for 24 h. The solution was filtered using 42 Whatman filter paper and rinsed with double distilled water several times to attain neutral pH. Then the biosorbent was dried at room temperature and finally in electric oven at 105°C till complete dryness. About 50 g, HNO_3 treated biosorbent was added to 1 L of $CaCl_2$ (0.1 M) solutions (for 24 h), filtered with 42 Whatman, and rinsed with distilled water to remove the unreacted amount of $CaCl_2$ (if any). The biosorbent was dried at room temperature and again placed in oven at 105°C to remove the left over moisture. CMBVL was

stored in the closed bottle till further use. HNO_3 treatment remove existing metal ions from biosorbent surface, while $CaCl_2$ treatment load calcium ions on biosorbent surface, which follow ion-exchange method for the removal of toxic heavy metal ions [19].

2.2. Characterization of biosorbent

The Barrett–Joyner–Halenda (BJH), Brunauer–Emmett–Teller (BET) surface area, pore diameter, and volume were analyzed by pore size and surface area analyzer (NOVA 2000e, Quantachrome USA). The surface morphology was studied by scanning electron microscopy (SEM) at fixed voltage of 10 kV. To determine the functional groups responsible for biosorption, Fourier transformed infrared spectroscopy (FTIR) (Perkin Elmer, Waltham, USA) in the frequency range of 400–4,000 cm^{-1} was used.

2.3. Effect of different experimental parameters

The effect of experimental parameters on biosorption such as pH (2–7), contact time (10–120 min), initial metals ion concentration (20–500 mg/L), adsorbents dosage (1–30 g/L), and temperature (298–323 K) were studied using batch experiment. Metals ion solutions with different concentrations were prepared by diluting stock solutions (1,000 mg/L) of Pb(II), Cd(II) and Cr(VI) with double distilled water. The pH of the solutions was adjusted either with 0.1 M HCl or NaOH solution. In each batch experiment, 250 mL conical flask containing 100 mL solutions of a given concentration were mixed with 0.5 g/L of CMBVL except for the investigation of biosorbent dosage and shacked in a temperature-controlled speed shaker at 130 rpm for specific interval of time. The solutions were filtered through Whatman No. 42 filter paper. Filtered solutions were analyzed for the remaining metal ion concentrations, by atomic absorption spectrophotometer. All the experiments were carried out in triplicate and their mean are presented. The amount of Pb(II), Cd(II) and Cr(VI) biosorbed (q_e in mg/g) and percent removal (%R) was calculated using the following equations [20].

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

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

where q_e (mg/g) is equilibrium biosorption capacity, V is the volume of metals ion solution in a liter, C_i and C_f are the initial and final metals ion concentration, and m mass of biosorbent in g.

2.4. Equilibrium studies

The equilibrium experiments were conducted in concentration range of 20–500 mg/L and other parameters such as contact time, pH, biosorbent dose, temperature, and shaking speed were kept constant. Their q_e values were calculated using Eq. (1) and plotted against initial

concentration. Langmuir and Freundlich isotherms were applied to analyze the adsorption equilibrium data.

2.5. Kinetic studies of heavy metals biosorption

To determine the effect of contact time of Pb(II), Cd(II) and Cr(VI) biosorption on CMBVL, a given concentration of metals were contacted with fixed amount of biosorbent for 10–120 min, while other experimental parameters were kept constant. Pseudo-first and pseudo-second-order kinetics models were employed to determine the kinetics parameters.

2.6. Thermodynamics of selected metal biosorption

To determine thermodynamics of Pb(II), Cd(II) and Cr(VI) biosorption on CMBVL, the experiments were carried out at 25°C, 30°C, 40°C, and 50°C, keeping all other optimum parameters constant. The Van't Hoff equation was applied to determine thermodynamic parameters.

3. Results and discussion

3.1. Characterization of CMBVL biosorbent

3.1.1. FTIR study of CMBVL before and after heavy metal biosorption

The FTIR spectra of CMBVL before and after Pb(II), Cd(II) and Cr(VI) biosorption are shown in Figs. 1a–d. The FTIR spectrum of CMBVL biosorbent in Fig. 1a shows various functional groups on its surface. The peak at 3,334 cm^{-1} indicates OH group [21]. The peak value 2,916 cm^{-1} shows the presence of CH_3 [22]. The peak at 1,635 cm^{-1} shows the existence of C=C [21]. The C–O stretching bond is at 1,099 cm^{-1} [22]. The peak value at 1,446 and 1,157 cm^{-1} shows the bending vibration of –NH and wagging vibration of $–CH_3$ group [23]. The FTIR spectrum of Pb(II) treated CMBVL Fig. 1b, indicates variation in peaks value. The peak at 3,334 cm^{-1} has been shifted to 3,332 cm^{-1}. The change in the frequency shows
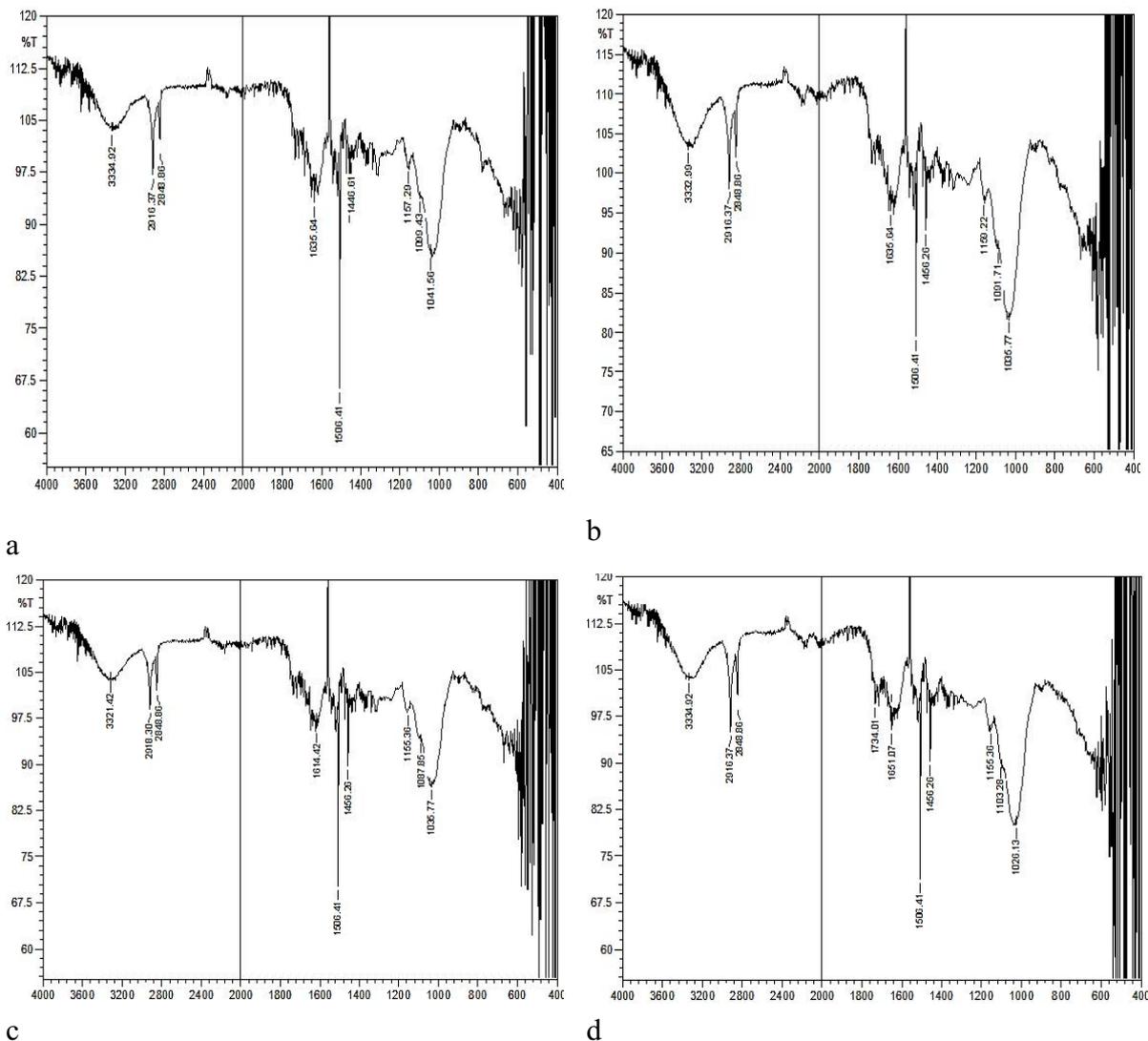
Fig. 1. FTIR spectrum of (a) CMBVL and (b) Pb(II) loaded CMBVL. FTIR spectra of (c) Cd(II) loaded CMBVL and (d) Cr(VI) loaded CMBVL.

the biosorption of Pb(II) on CMBVL. The FTIR spectra of Cd(II) biosorbed on CMBVL Fig. 1c, shows some changes in the peak values. The peaks at 3,334 cm^{-1} for OH has shifted to 3,321 cm^{-1} while the –CH$_3$ at 2,916 cm^{-1} have been shifted to 2,918 cm^{-1}. The difference in the peaks values indicates that –OH and –CH group shows contribution in the biosorption of Cd(II) on CMBVL. The FTIR spectrum of Cr(VI) treated CMBVL, Fig. 1d shows some variation. The peak at 1,099 cm^{-1} was shifted to 1,026 cm^{-1}. The peak at 1,635.64 cm^{-1} also shifted to 1,651 cm^{-1}. The change in stretching frequency of peak values of C=O group, –OH group, and C=C group confirm the biosorption of Cr(VI).

3.1.2. Surface area, pore diameter, and pore volume

The most common method used to measure the surface area of biosorbent is BJH and BET method. The specific surface area of a biosorbent is determined by physical biosorption of a N$_2$ gas on the surface of the biosorbent and by calculating the amount of biosorbed gas corresponding to a monomolecular layer on the surface the surface area is determined. The data reveal that CMBVL has a larger surface area with better porosity which would be a good biosorbent in terms of high biosorption capacities. The BJH and BET surface area, pore diameter, and volume of CMBVL is given in Table 1.

Table 1
Surface area, pore diameter, and pore volume of CMBVL biosorbent

Biosorbent	CMBVL
BJH surface area (m^2/g)	284.74
BET Surface area (m^2/g)	69.06
Pore diameter (Å)	128.06
Pore volume (cc/g)	0.96

3.1.3. SEM images

Surface morphology of biosorbent was studied by SEM as shown in Figs. 2a and b. Prior to treatment, the biosorbent surface was smooth which indicates an unsuitable surface for biosorption of metals ions. After treatment, it is clear from the SEM image that the irregular, rough, shattered edges, and crooks on the surface make the material suitable for Pb(II), Cd(II) and Cr(VI) biosorption.

3.2. Effect of heavy metals concentration

The effect of initial metals ion concentration biosorption on CMBVL were studied at pH 3, 7, and 2 respectively for Pb(II), Cd(II) and Cr(VI), contact time (90 min), biosorbent optimized dosage (5 g/L) for a wide concentration range (20–500 mg/L) as shown in Fig. 3. It is clear from Fig. 3 that heavy metals ion biosorption on CMBVL (q_e) increases with increasing initial metal ions concentration. At lower metal ions concentration, the ratio of metal ions competing for the available active sites on the CMBVL is smaller, and subsequently, the biosorption process becomes independent of the initial concentration. At a higher concentration of metal ions, the available active sites for biosorption become fewer as compared to the number of metal ions present and hence biosorption process depends on initial concentration. This behavior results in the saturation of biosorbent sites. The initial concentration provides an important driving force to overcome all mass transfer resistance of metals ion between aqueous solution and solid phases. Hence, a higher initial concentration of metal ions increases the rate of biosorption [23,24].

3.3. Effect of contact time on heavy metals biosorption

Effect of contact time on the biosorption of heavy metal ions biosorption on CMBVL were studied in the range of 5–120 min (Fig. 4). The batch biosorption experiments

(a)

(b)
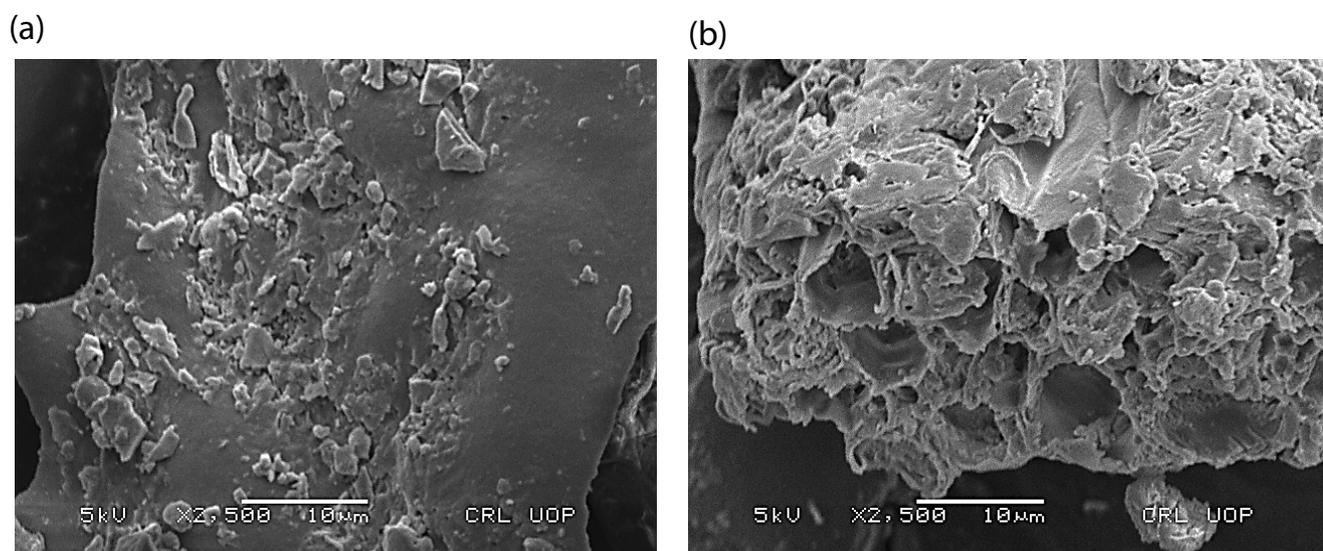
Fig. 2. SEM image (a) before treatment and (b) after chemical treatment.
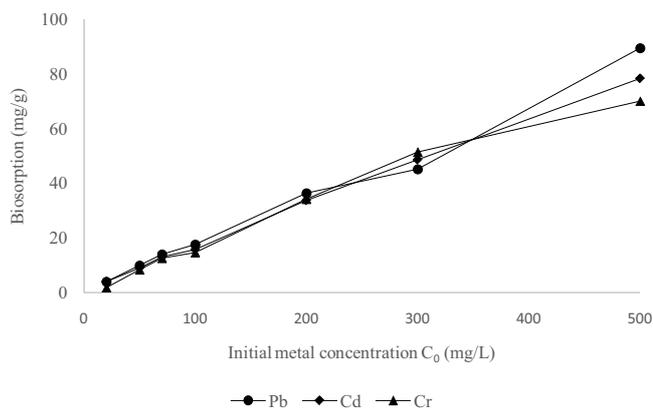
Fig. 3. Pb(II), Cd(II) and Cr(VI) concentration effect on biosorption capacity.

Fig. 5. Effect of solution pH on Pb(II), Cd(II) and Cr(VI) biosorption.

surface leading to strong attraction between positively charged groups on CMBVL surface and chromate ions [27–29].

3.5. Effect of biosorbent dosage

Biosorbent dosage effect is a significant experimental factor for biosorption. To study this effect, various amount of CMBVL in the range 1–30 g/L as shown in Fig. 6 were contacted with fixed concentrations of metal ions. As it is clear from the graphs that biosorption rate of Pb(II), Cd(II) and Cr(VI) increases with the increase of CMBVL dose. The results showed that 5 g/L of CMBVL was found to be an optimum dosage.

Fig. 4. Contact time effect on Pb(II), Cd(II) and Cr(VI) biosorption on CMBVL.

3.6. Equilibrium studies of heavy metals biosorption

Isotherm models such as Langmuir and Freundlich were applied to determine the characteristic biosorption parameters and explain the observed biosorption behavior.

were performed using fixed volume (100 mL) of each metal ions, optimum biosorbent dosage (0.5 g/L of CMBVL), and optimum pH for Pb(II), Cd(II) and Cr(VI) were 3, 2, and 7, respectively, with shaking speed of 130 rpm. The analysis shows that biosorption of 87%, 80%, and 66% for Pb(II), Cd(II) and Cr(VI) was obtained in 20 min. After that, a small change was observed till 75 min and then no prominent changes at the same concentration were observed.

3.6.1. Langmuir isotherm

The Langmuir isotherm refers to monolayer biosorption on to a surface containing a finite number of active sites of uniform diameters with no transmigration of sorbate on the surface. Once a site is saturated no further biosorption takes place on that active site. The linear form of Langmuir isotherm is given as [30]:

3.4. Effect of pH on biosorption

The pH of solution plays an important role in the biosorption of a metal by any sorbent as it influences the polarity of the biosorbent and ionic mobility. To study the effect of pH on the removal of Pb(II), Cd(II) and Cr(VI) by CMBVL the solutions pH was kept in the range 2–7 for selected metals (Fig. 5). Maximum removal of Pb(II) occurred at pH 3 while that of Cd(II) and Cr(VI) at pH 7 and 2, respectively [25,26].

Unlike Pb and Cd, the maximum biosorption for Cr(VI) occurred at pH 3.0. At low pH, the Cr is predominately in the form of $HCrO_4^-$ ions. Maximum biosorption at lower pH is likely to be favored by more H^+ ions on the CMBVL

$$\frac{C_e}{q_e} = \frac{1}{R_L q_m} + \frac{C_e}{q_m} \qquad (3)$$

In Eq. (3), q_e stands for quantity of metal biosorbed at equilibrium (mg/g), C_e is concentration at equilibrium (mg/L), q_m represents maximum biosorption capacity of CMBVL (mg/g), K_L is a constant related to biosorption energy.

The plot C_e/q_e vs. C_e gives a straight line (Fig. 7) with q_m and $1/R_L$ as slope and intercept, respectively. The R_L values shows that the biosorption process is favorable when $0 < R_L < 1$, undesirable when $R_L > 1$, linear when $R_L = 1$ or irreversible when $R_L = 0$. The values obtained for Pb(II), Cd(II) and Cr(VI) were 0.638, 0.115, and 0.025, respectively which shows that the biosorption process were desirable [31–33].
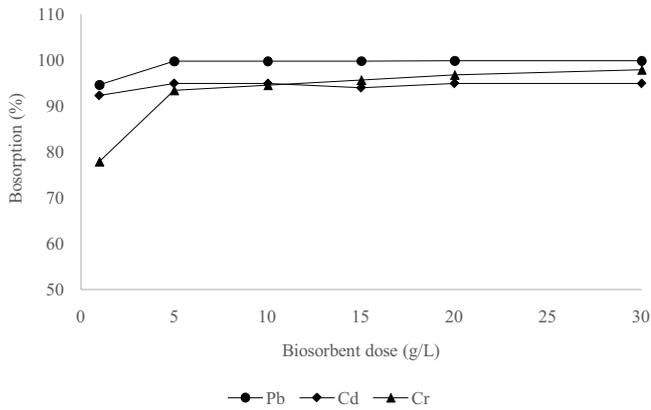
Fig. 6. Effect of CMBVL dose on Pb(II), Cd(II) and Cr(VI) biosorption.

The R^2 values calculated from Fig. 7 for Pb(II), Cd(II) and Cr(VI) were 0.999, 0.995, and 0.982, respectively, as shown in Table 2. Also from greater correlation co-efficient (R^2) for Pb(II), Cd(II) and Cr(VI), it was concluded that the best fit of the data could be obtained with Langmuir isotherm as compare to Freundlich isotherm model.

3.6.2. Freundlich isotherm

Freundlich isotherm is related with the multilayer biosorption and explains the interactions among the molecules biosorbed. The Freundlich isotherm model is linearized form is given as below [34]:

$$\ln q_e = \log K_F + \frac{1}{n}\ln C_e \tag{4}$$

In Eq. (4), q_e represents the amount of metal adsorbed per unit mass of CMBVL at equilibrium (mg/g). K_F is Freundlich constant and n is an empirical factor dealing with the strength of biosorption. The values of K_F and n were obtained from slope, intercept of $\ln q_e$ vs. $\ln C_e$ plot as shown in Fig. 8, and are given in Table 2.

3.7. Kinetics study

Pseudo-first-order and second-order models were applied to determine the kinetic mechanism of Pb(II), Cd(II) and Cr(VI) biosorption on CMBVL.

3.7.1. Pseudo-first-order equation

In 1898, Lagergren presented the first-order model in order to explain biosorption kinetic on solid surface. The pseudo-first-order equation is given in its linearized form as below [35]:

$$\ln\left(q_e - q_t\right) = \ln q_e - K_1 t \tag{5}$$

In Eq. (5), K_1 is the first-order rate constant for biosorption, q_e and q_t are the amounts of heavy metals biosorbed per unit mass of CMBVL at equilibrium and time t,

Table 2
Langmuir and Freundlich constants for Pb(II), Cd(II), and Cr(VI) biosorption on CMBVL

Isotherm models	Parameters	Cations		
		Pb(II)	Cd(II)	Cr(VI)
Langmuir	q_{max} (mg/g)	78.740	117.647	69.930
	R_L (L/mg)	0.638	0.115	0.025
	R^2	0.999	0.995	0.982
Freundlich	K_F (L/mg)	8.842	1.241	2.131
	n	1.987	1.119	1.332
	R^2	0.998	0.993	0.980
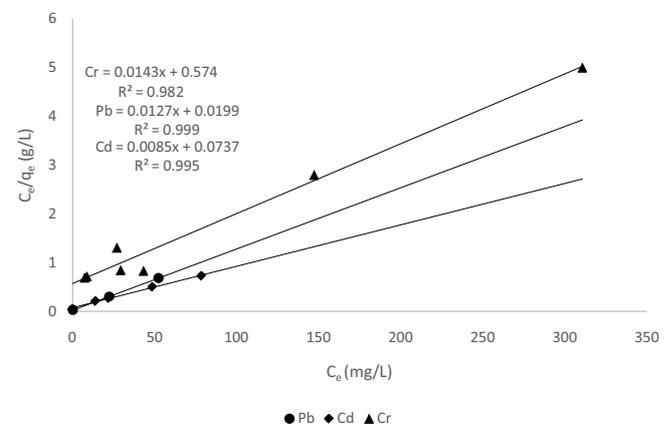
Fig. 7. Langmuir isotherm for Pb(II), Cd(II) and Cr(VI) biosorption on CMBVL.

respectively. The $\ln(q_e - q_t)$ against t were plotted for Pb(II), Cd(II) and Cr(VI) and the value of q_e and K_1 for all three metals were calculated from the slope and intercept as shown in Fig. 9 and their numerical values are presented in Table 3.

3.7.2. Pseudo-second-order equation

The pseudo-second-order model deals with chemisorption (involving the sharing of electrons between sorbate and biosorbent). The pseudo-second-order equation can be represented in the linearized form as [36]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

In Eq. (6), K_2 is pseudo-second-order rate constant (g/mg min). The t/q_t vs. time t were plotted for Pb(II), Cd(II) and Cr(VI), the values of q_e and K_2 were calculated from the slope and intercept as shown in Fig. 10 and are given in Table 3. Based on R^2 values it was concluded that biosorption of Pb(II), Cd(II) and Cr(VI) on CMBVL prefers to follow pseudo-second-order kinetic model as compared to first-order kinetic model. Moreover, the empirical q_e value agrees with the calculated values obtained from the linear form of the pseudo-second-order model.
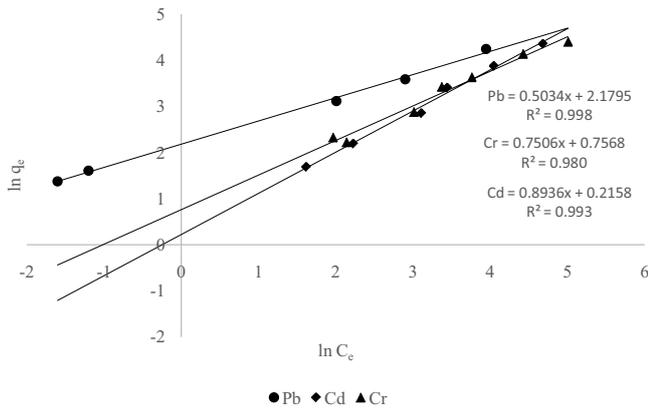
Fig. 8. Freundlich isotherm for Pb(II), Cd(II) and Cr(VI) biosorption on CMBVL.
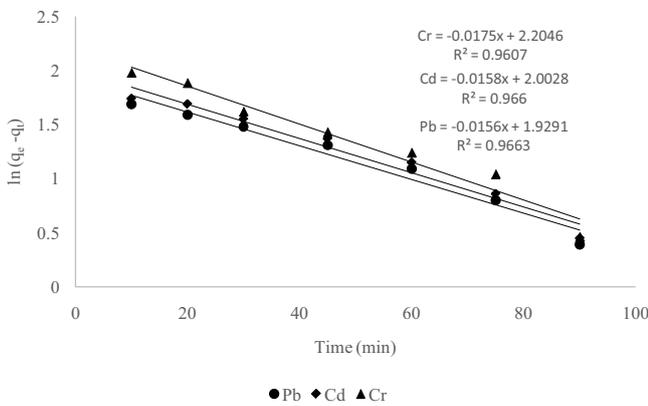
Fig. 9. Pseudo-first-order kinetic plot for Pb(II), Cd(II) and Cr(VI) biosorption.
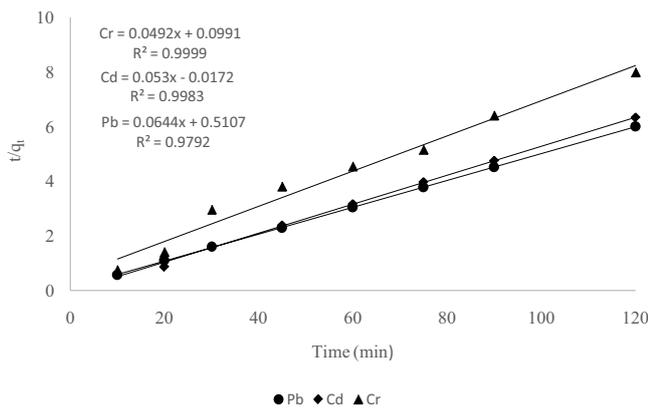
Fig. 10. Pseudo-second-order kinetic plot for Pb(II), Cd(II) and Cr(VI) biosorption.

3.7.3. Intraparticle diffusion equation

The intraparticle diffusion equation was applied in order to decide the rate-controlling steps of Pb(II), Cd(II) and Cr(VI) biosorption on CMBVL. The linearized form of intraparticle diffusion equation can be presented as follow [37]:

Table 3
Pseudo-first and second-order kinetics parameter of Pb(II), Cd(II) and Cr(VI) biosorption on CMBVL

Kinetic models	Parameters	Cations		
		Pb(II)	Cd(II)	Cr(VI)
Pseudo-first-order	K_1 (1/min)	0.0156	0.0158	0.0175
	q_e (mg/g)	0.657	0.694	0.790
	R^2	0.9663	0.966	0.9607
Pseudo-second-order	K_2 (g/mg min)	0.0631	1.541	0.248
	q_e (mg/g)	15.528	18.868	20.325
	R^2	0.9792	0.9983	0.9999
Intraparticle diffusion	K_{diff} (mg/g min$^{1/2}$)	0.5576	0.5108	1.1627
	C (mg/g)	16.063	15.531	9.4573
	R^2	0.8706	0.6687	0.9894

$$q_t = K_{diff} t^{1/2} + C \qquad (7)$$

where q_t (mg/g) is the quantity of Pb(II), Cd(II) and Cr(VI) biosorbed on the CMBVL at any time, K_{diff} (mg/g min$^{1/2}$) denotes a constant while C (mg/g) is intercept related to the thickness of boundary.

By plotting q_t of Pb(II), Cd(II) and Cr(VI) against $t^{1/2}$, a curve as shown in Fig. 11 can be obtained. The values of slope K_{diff} and intercept C are shown in Table 3.

The linear portions of these curves do not pass through the origin of the graph, indicating that intra-particle diffusion is not the only rate-controlling step for the biosorption of these metals on the prepared biosorbent.

3.8. Thermodynamics of biosorption

The Van't Hoff equation was applied to calculate $\Delta H°$ and $\Delta S°$ for Pb(II), Cd(II) and Cr(VI) biosorption on CMBVL [38]:

$$\ln K = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \qquad (8)$$

In Eq. (7), K is a constant concerning to the amount of Pb(II), Cd(II) and Cr(VI) biosorbed per unit mass of CMBVL. The term $\Delta S°$ stands for entropy change while $\Delta H°$ represents enthalpy change. R is the universal gas constant and its value is 8.314 kJ/mol and T is the temperature in Kelvin scale. The value of $\Delta H°$ and $\Delta S°$ were calculated by plotting $\ln K$ vs. $1/T$ for Pb(II), Cd(II) and Cr(VI) as shown in Fig. 12 and are given in Table 4. The values of $\Delta H°$ are negative and that of $\Delta S°$ are positive indicates the exothermic and spontaneous nature of the biosorption process. The values of Gibbs free energy change $\Delta G°$ at different temperatures were calculated using the equation:

$$\Delta G° = \Delta H° - T\left(\Delta S°\right) \qquad (9)$$

The negative values of $\Delta G°$ correspond to the favorability of Pb(II), Cd(II) and Cr(VI) biosorption on CMBVL as given in Table 4.

In Table 4, the values of $\Delta H°$ and $\Delta G°$ are negative while that of $\Delta S°$ is positive, indicating the exothermic and spontaneous nature of the adsorption process.

3.9. Comparison of biosorption capacity of present biosorbent with reported biosorbents

A comparison has been provided in the following Table 5, clearly indicating that this biosorbent has high biosorption capacity and could be used as efficient precursors for removal of heavy metals from wastewater.

4. Conclusion

Biosorption of metals ion such as Pb(II), Cd(II) and Cr(VI) from aqueous solution by CMBVL was studied. The FTIR spectra of CMBVL shows the presence of hydroxyl, alkene, and amine functional groups. The FTIR
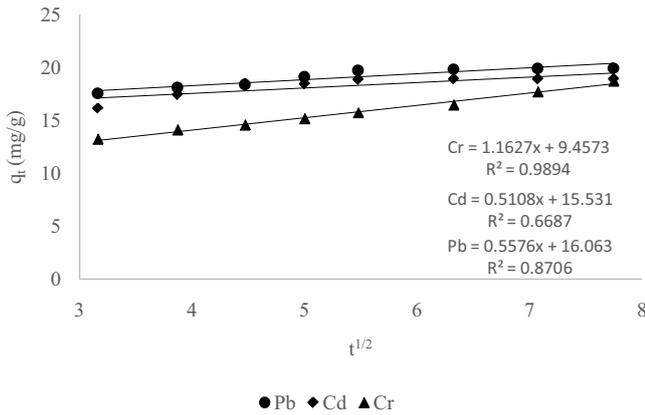
Fig. 11. Intraparticle diffusion kinetic plot for Pb(II), Cd(II) and Cr(VI) biosorption.
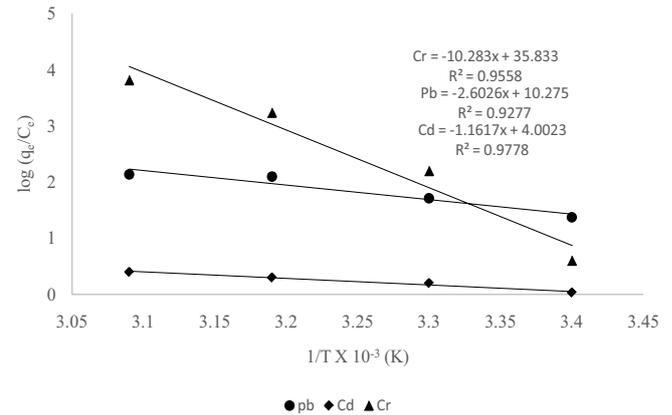
Fig. 12. Thermodynamic parameters for Pb(II), Cd(II) and Cr(VI) biosorption.

Table 4
Thermodynamic parameters of Pb(II), Cd(II), and Cr(VI) biosorption on CMBVL

Cations	$\Delta H°$ (kJ/mol)	$\Delta S°$ (kJ/mol)	$\Delta G°$ (kJ/mol)			
			298 K	303 K	313 K	323 K
Pb(II)	−21.638	85.424	−25.435	−25.862	−26.717	−27.571
Cd(II)	−9.658	33.275	−9.906	−10.073	−10.405	−10.788
Cr(VI)	−85.833	297.915	−88.693	−90.183	−93.161	−96.141

Table 5
Comparison of biosorption capacity (mg/g) of CMBVL with other reported biosorbents for the removal of Pb(II), Cd(II) and Cr(VI)

Biosorbents	q_{max}			Reference
	Pb(II)	Cd(II)	Cr(II)	
This research work	78.74	117.65	69.93	CMBVL
Ulva lactuca	34.7	29.2	–	[39]
Cephalosporium aphidicola	36.9	–	–	[40]
Phanerochaete chrysosporium	69.8	23.0	–	[41]
Rhizopus arrhizus	15.5	–	–	[42]
Zoogloea ramigera	10.5	–	–	[43]
Mucor rouxii	–	20.3	–	[43]
Rhizopus arrhizus	–	26.8	–	[44]
Phanerochaete chrysosporium	–	15.2	–	[45]
Quercus ithaburensis	–	–	62.76	[14]
Quercus dilate	16.09	6.13	2.19	[46]
Horticultural peat	36.49	10.57	6.80	[47]

spectra of Pb(II), Cd(II) and Cr(VI) loaded confirm the biosorption of all three metals ion. The surface area and SEM studies indicate greater surface area and porous structure of CMBVL after chemical treatment. Batch biosorption experiments were used for analyzing the effects of variables such as initial metal ions concentration, contact time, pH, and biosorbent dosage. The Langmuir isotherm model is the best fit to the experimental data for all the three metal ions, with the maximum biosorption capacities of 78.740, 117.647, and 69.930 mg/g for Pb(II), Cd(II) and Cr(VI) ions, respectively. Kinetic studies demonstrated that the mechanism for biosorption Pb(II), Cd(II) and Cr(VI) followed the pseudo-second-order model. Maximum biosorption of Pb(II), Cd(II) and Cr(VI) occurred at pH 3, 5, and 2, respectively. At pH higher than 7, metals ion precipitation occurs rather than biosorption. The negative $\Delta H°$ and $\Delta G°$ values depicted that the biosorption of Pb(II), Cd(II) and Cr(VI) on CMBVL were exothermic and feasible process. The positive $\Delta S°$ values indicate spontaneous nature. On the basis of all results, it can be concluded that CMBVL can be effectively used for the biosorption of Pb(II), Cd(II) and Cr(VI) from an aqueous solution using the batch biosorption method.

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