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Plant-mediated detoxification of lead, cadmium, and chromium present in aqueous solution through chemically modified *Populus nigra* leaves

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ABSTRACT

In this study, a low-cost biosorbent was prepared using *Populas nigra* leaves as biomass. The leaves were modified chemically by nitric acid/calcium chloride and characterized through different instrumental techniques (Fourier transformed infrared spectroscopy, scanning electron microscopy and surface area analyzer). The prepared biosorbent was used as adsorbent for the removal of Cd(II), Cr(VI) and Pb(II) ions from aqueous media. Biosorption was studied as a function of pH (2–7), biosorbent dose (1–30 mg/L), contact time (5–120 min), and initial metal ion concentration (20–700 mg/L) at a shaking speed of 170 rpm. The experimental isothermal data were analyzed by the Langmuir and Freundlich isotherm models. The maximum monolayer biosorption capacity of Cd(II), Cr(VI), and Pb(II) was found to be 107.526, 208.3, and 172.413 mg g^{-1}, respectively, with best fitting obtained for Langmuir model. Kinetic data fitted well to the pseudo-second order equation rather than the pseudo-first order equation. The thermodynamic parameters such as standard enthalpy change ($\Delta H°$), entropy change ($\Delta S°$), and Gibbs free energy ($\Delta G°$) determined suggest that biosorption of these metals by this biosorbent is an exothermic, spontaneous and favorable process.

Keywords: Biosorption; Langmuir isotherm; Freundlich isotherm; Thermodynamic parameters; Kinetic models

1. Introduction

Contamination of aqueous environment with heavy metals, released from industries, is a severe environmental threat that needs precautionary measures to be taken on part of government and environmental agencies [1]. Cadmium is released by different industries such as phosphate fertilizer, metal plating, mining, pigments, smelting, batteries, etc. According to World Health Organization (WHO), the maximum permissible limit reported for cadmium is 0.005 mg/L [2]. Cadmium concentration beyond

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this limit will cause muscular cramps, chronic pulmonary cramps, nausea, salivation, diarrhea, skeletal deformation, and renal degradation. Cadmium also has the capability to replace Zn(II) from metallo-enzymes, which is an essential component for their catalytic activities [3,4]. Chromium is discharged from industries such as paints, dyes, pigments, electroplating, textiles, leather tanning, metal finishing, and chromate preparation [5]. Chromium may be present in several oxidation states but only Cr(III) and Cr(VI) are stable and occur in the aqueous environment. The Cr(VI) form is more toxic than the Cr(III) [6]. The maximum tolerable limit reported by WHO for Cr(VI) is 0.05 mg/L in drinking water. Inhalation of Cr(VI) containing material can be harmful to internal organs [7]. Skin contact of Cr(VI) compounds causes skin diseases [8]. The sources releasing lead into the aqueous environment include matches, glasses, oil refineries, and pigment industries [9]. Lead causes liver and kidney diseases, brain damage, and finally death, when present beyond permissible level of 0.010 mg/L [10].

The conventional techniques used for the removal of heavy metals from aqueous environment include adsorption, ion exchange, membrane separation, chemical precipitation, solvent extraction, and reverse osmosis [11]. The economical and effective nature of adsorption make this technique more important than others while removing the heavy metals from aqueous environment [12]. Recently, many biosorbent prepared from waste biomass such as agriculture waste, food organic waste, fungi, bacteria, algae, etc. have been tested for the removal of toxic heavy metals from aqueous environment [13].

Populus nigra is commonly known as black poplar that grows in almost all continents. It is a medium to tall-sized deciduous plant, reaching to a height of 20–30 m, while their trunk reaches up to 1.5 m in diameter. Yu et al. [14] has used its bark as adsorbent for the reclamation of heavy metals from water. Apart from its uses as adsorbent, Jayamani et al. [15] has reported its potential role as bio accumulator of heavy metals. Different biomass have different phytochemical compositions with varied functionalities and thus having different potentials of binding heavy metals if converted into adsorbent. Keeping in view the mentioned fact, the *Populus nigra* leaves were converted into an efficient adsorbent. To the best of our knowledge, the leaves of this plant has not been used as biosorbent for the removal of heavy metals from water.

In current research work, biosorbent was prepared from *Populus nigra* leaves, chemically modified by HNO_3/$CaCl_2$ and was used to remove Cd(II), Cr(VI) and Pb(II) from aqueous environment. The effect of experimental conditions such as heavy metal concentration, contact time, pH of solution, and biosorbent dosage was also evaluated.

2. Materials and methods

2.1. Biosorbent collection and synthesis

Mature *Populus nigra* leaves were collected from District Peshawar, KPK Pakistan. The leaves were collected in clean polythene bags, washed two times with double distilled water to remove dust particles and soluble impurities, stored in shade for 2 weeks till dryness and then in electric oven at 46°C until the leaves become crispy. The crispy leaves were powdered and passed through a 44-mesh sieve. The fine powders were washed several times with double distilled water to get rid of any color, finally oven dried at 70°C and stored in air-tight bottles till further use at 4°C.

2.2. Biosorbent chemical modification

About 100 g of 44-mesh powders were treated with 2 L of HNO_3 (0.1 M) for 24 h with continuous shaking, followed by filtration through 42 Whatman filter paper and washed with double distilled water till neutral pH. About 50 g of dried HNO_3 treated sample was treated with 1 L of $CaCl_2$ (0.1 M) following same procedure as mentioned (HNO_3 treatment). The chemical treatment usually enhances the removal efficacies of heavy metals of biosorbents.

2.3. Characterization of prepared biosorbent

The Fourier transformed infrared spectroscopy (FTIR) spectrophotometer (PerkinElmer, Waltham, Massachusetts, USA, Model 2000 with KBr discs) was used to determine the functional groups present on CMPNL surface before and after loading heavy metals. The samples were scanned in range of 400–4,000 cm^{-1}. Pellets were prepared by pressing mixing 0.3 g of KBr and 0.003 g of biosorbent at 3–7 bar pressure. The surface texture of prepared biosorbent was visualized through scanning electron microscope (JEOL, Japan-JSM 5910) under a set up voltage of 10 kV. The Barrett–Joyner–Halenda (BJH), Brunauer–Emmett–Teller (BET) surface area, pore volume, and pore distribution were investigated using surface area analyzer (NOVAS200e, Quantachrome, USA).

2.4. Batch biosorption experiments

The effect of experimental conditions, which affects heavy metal biosorption such as pH (2–7), initial heavy metals concentration (20–700 mg/L), contact time (5–120 min), biosorbent dosage (1–30 g/L) and temperature (293–333 K) were studied using batch experiments. Working solution of Cd(II), Cr(VI) and Pb(II) having different concentrations was prepared by diluting their stock solutions with double distilled water. The pH of the solutions was adjusted to the required value (2–7) by adding either HCl (0.1 M) or NaOH (0.1 M) solutions. In each batch experiment, 100 mL of Cd(II), Cr(VI), and Pb(II) having required concentrations contained in 250-mL conical flasks were mixed with 5 g/L of CMPNL except for the investigation of biosorbent dosage and shaken in a shaking water bath at 170 rpm for specified interval of time. The slurries after adsorption experiments were filtered through Whatman no 42 filter paper and remaining metal ion concentration in filtrates were determined using an atomic absorption spectrophotometer. The amount of Cd(II), Cr(VI), and Pb(II) biosorbed q_e (mg/g) and percentage removal (%R) of heavy metals were calculated using the following equations:

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

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

where C_i and C_f are the initial and final concentration of Cd(II), Cr(VI) and Pb(II), V is volume of solution (L) while m is mass of CMPNL biosorbent.

2.5. Effect of heavy metals concentration

To study the effect of heavy metals concentration on biosorption, the biosorbent adsorption capacities were evaluated in range; 20–700 mg/L of selected heavy metals. Other optimum parameters such as pH, contact time, biosorbent dosage, and temperature were kept constant. Freundlich and Langmuir isotherm models were applied to explain the obtained equilibrium data.

2.6. Effect of contact time

The effect of contact time on biosorption of heavy metals was evaluated for an interval of 0–120 min. Other optimum parameters mentioned above were kept constant. Pseudo-first order and second order kinetic equations were applied to calculate the kinetic parameters and decide the best model between them. Intra-particle diffusion model was used to explain the adsorption mechanism.

2.7. pH and biosorbent dosage effect

The biosorption of heavy metals on CMPNL was studied in acidic pH range (pH 2–7) as at basic pH these metals form precipitates. The solution pH was adjusted by HNO_3 (0.1 M) and NaOH (0.1 M). The biosorbent dose effect was analyzed from 1 to 30 g/L. Other experimental conditions were same as mentioned above.

2.8. Thermodynamic study

To determine thermodynamics parameters of Cd(II), Cr(VI), and Pb(II) biosorption on CMPNL, fixed concentrations of metals in 100 mL flasks were contacted with fixed amount of biosorbent and shaken at 20°C, 30°C, 40°C, and 50°C for specified interval of time. Van't Hoff equation was applied to analyze the data obtained.

3. Results and discussions

3.1. Characterization of biosorbent

3.1.1. Fourier transformed infrared spectroscopy

FTIR spectra of CMPNL loaded with selected metals and unloaded are shown in Figs. 1a–d. The FTIR spectra of unloaded CMPNL shows a clear broad band at 3,332.99 cm^{-1}, which indicates OH group (stretching vibration) [16]. The C–H stretching peak is present at 3,000 cm^{-1} indicating the presence of compounds of non-aromatic nature [17]. Peak at 1,099 cm^{-1} is due to C–O group present [17]. A broad band at 1,028 cm^{-1} can be attributed to O–H; out of plane bending vibration [18]. A little broader and intense peak at 1,614 cm^{-1} is due to carbonyl group of carboxylic acid, which differ from the peak of ketone and aldehyde in the sense that peak of aldehydes and ketones is intense and sharper [19]. Fig. 2b shows Cd(II)-loaded CMPNL, the changes in the intensity and position of the peak are clearly observable. The peak at 3,332 cm^{-1} for OH has been shifted to 3,278 cm^{-1}. Peak at 1,614 cm^{-1} for carbonyl group of carboxylic acid has been moved to 1,616 cm^{-1}. Similarly, the peak at 1,510 cm^{-1} was moved to 1,519 cm^{-1}. The two peaks at 1,022 and 1,099 cm^{-1} after loading are almost mixed and as a result single broader peaks appear at 1,022 cm^{-1}. From these changes, we can conclude that O–H group of carboxylic acid is responsible for Cd(II) biosorption. Fig. 2c shows Cr(VI)-loaded CMPNL, similar peak shifts were observed after Cr(VI) biosorption on CMPNL. Fig. 2d shows Pb(II)-loaded CMPNL, the peak of Pb-loaded CMPNL at 3,332 cm^{-1} has shifted to 3,288 cm^{-1}. Similarly, the peak at 1,614 cm^{-1} has been shifted to 1,625 cm^{-1}. The peak at 1,519 cm^{-1} has disappeared after Pb(II) biosorption.

3.1.2. Scanning electron microscope

The SEM images of chemically modified biosorbent are shown in Figs. 2a and b. Fine changes were observed, when the *Populus nigra* leaves powder were treated with $CaCl_2$. The HNO_3-treated *Populus nigra* biosorbent initially was like an assembly of fine particles with indefinite shapes and sizes which after $CaCl_2$ treatment adopted definite shapes and sizes.

3.1.3. Surface area, pore volume and diameter

The BET surface area, and BJH pore volume and diameter of CMPNL are shown in Table 1. The table shows that CMPNL has greater surface area with better porosity, which makes it a good biosorbent in terms of biosorption capacity.

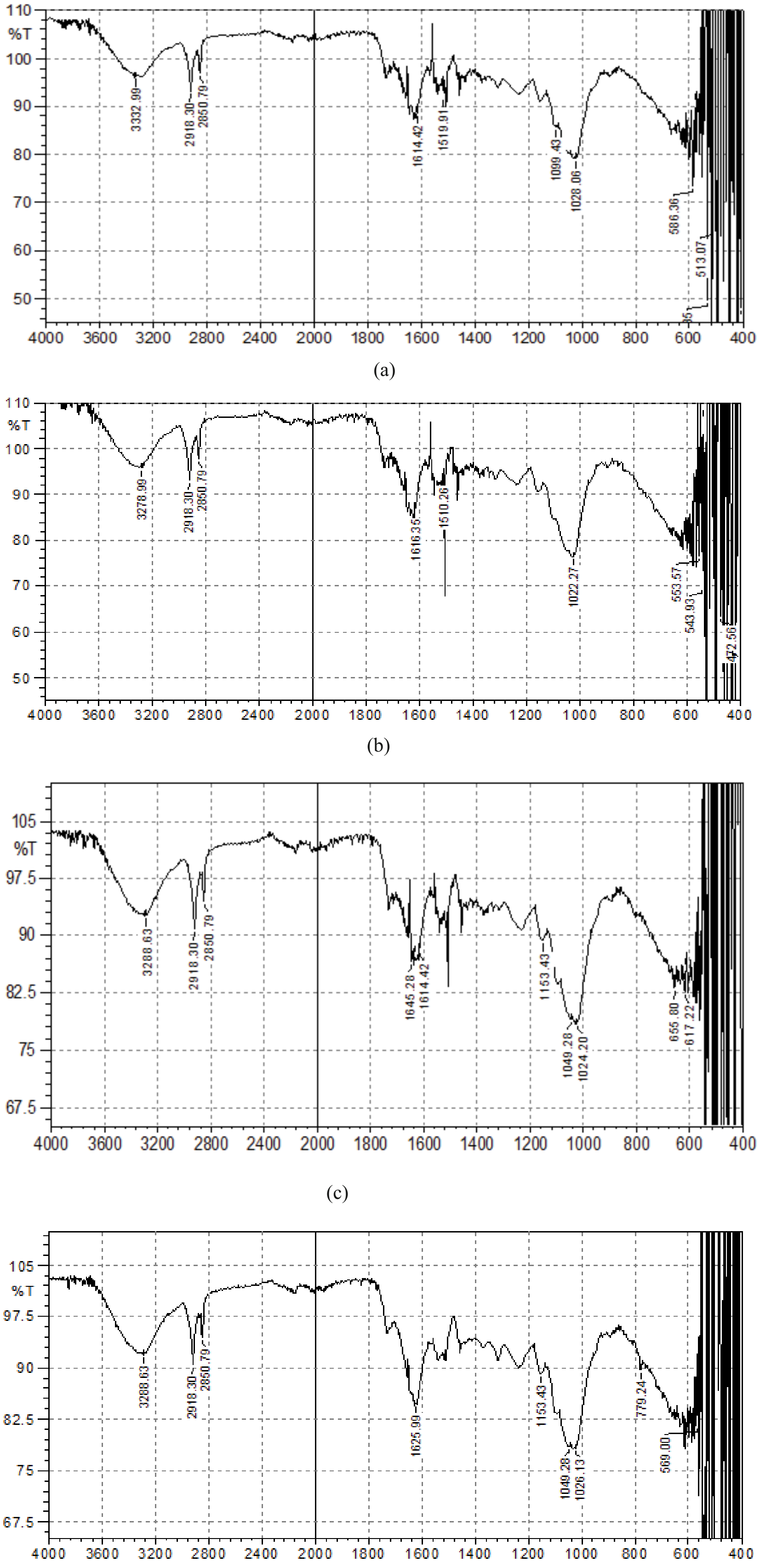
3.2. Batch biosorption experiments

3.2.1. Effect of heavy metals ion concentration

Effects of heavy metals ion concentration on biosorption were studied in concentration range of 20–700 mg/L. The results are shown in Fig. 3. At lower concentrations, the ratio of the metals ion relative to surface area is low and rapid biosorption thus occurred. However, later the biosorption became independent of metals ion concentration and the steepness of the curve is not so sharp as compared with the one observed at initial stages [20]. It was concluded from the observed data that biosorption (mg/g) increased with increasing metals ion concentration within the tested concentration range.

3.2.2. Effect of contact time on biosorption

The biosorption of selected heavy metals ions on CMPNL is shown in Fig. 4 showing it as a two-step process. The first step is fast in which maximum biosorption takes place while the second step is slow that ended on reaching to equilibrium as majority of active sites are occupied now and a steady state was reached. Similar observations



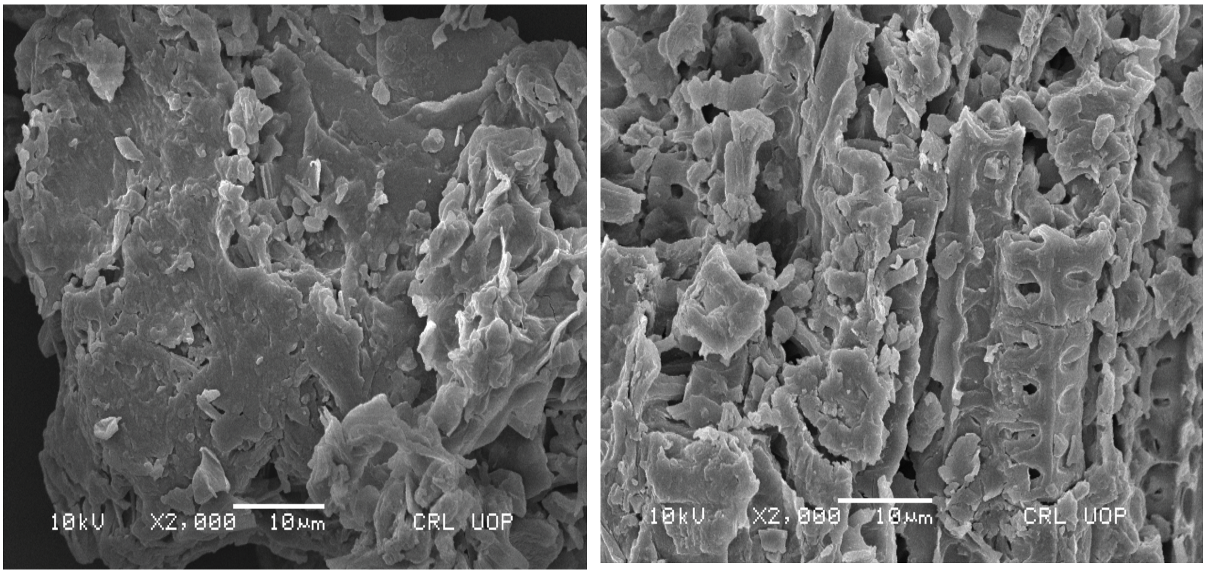
(a)

(b)

(c)

(d)

Fig. 1. FTIR spectra of CMPNL (a) unloaded, (b) loaded with Cd, (c) loaded with Cr and (d) loaded with Pb.



(a)

(b)

Fig. 2. SEM images of adsorbent (a) HNO_3-treated CMPNL and (b) HNO_3 + $CaCl_2$–treated CMPNL.

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

Surface area (BET) (m^2/g)	62.22
Pore volume (cc/g)	0.39
Pore diameter (Å)	128.04

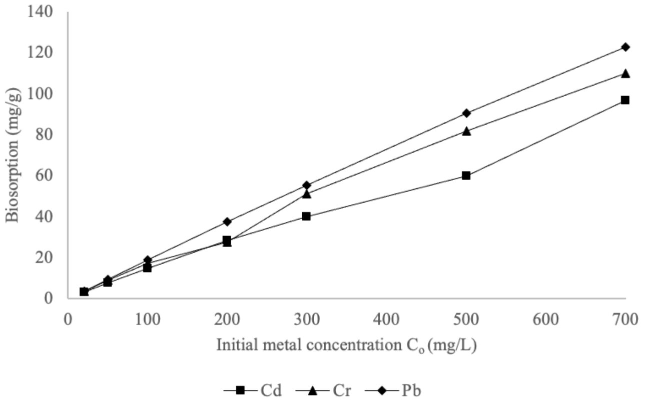


Fig. 3. Cd(II), Cr(VI), and Pb(II) concentration effect on biosorption.

by other researchers about biosorption of metals have also been documented previously [21].

3.2.3. Effect of pH on biosorption of selected metals

The effect on selected metals was studied in range from 2 to 7 (Fig. 5). Basic pH was not tested as at higher pH the metal forms precipitates. It is clear from figure that percentage biosorption of Cd(II), Cr(VI), and Pb(II) increases with increasing pH within the tested limit. The optimum pH recorded for Cd(II) and Pb(II) was 6 and 7, respectively, while for Cr(VI) the maximum biosorption was recorded at pH 2 and decreased with increasing pH [22]. At lower pH, the concentration of H^+ was high in aqueous solution and thus the binding sites became positively charged and positively charged metals such as Cd(II) and Pb(II) were repelled [23] that is why optimum pH is 6 and 7, respectively, for them. At higher pH, the surface becomes negatively charged and hence attract Cd(II) and Pb(II) ions [24]. In solution, when pH is lower than 2, chromium exists in the form of H_2CrO_4 but at pH 2–5 it may be present in the form of $HCrO_4^{-1}$ and $HCrO_7^{-2}$ as dominated species [23].

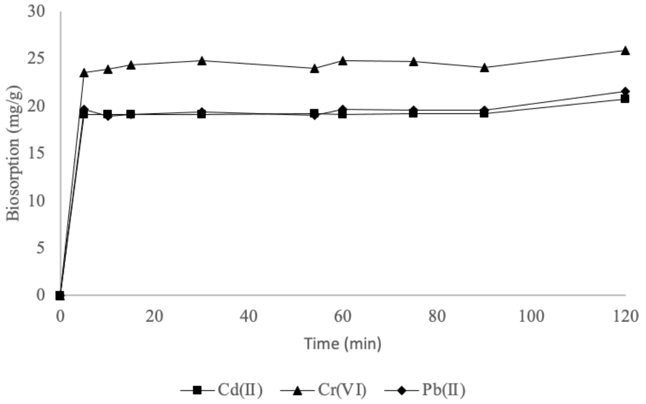


Fig. 4. Contact time effect of selected metals biosorption on prepared adsorbent.

3.2.4. Effect of biosorbent dosage on heavy metals biosorption

The effect of biosorbent dosage on heavy metal biosorption was studied by changing the quantity of biosorbent from 1 to 30 g/L and results are shown in Fig. 6.

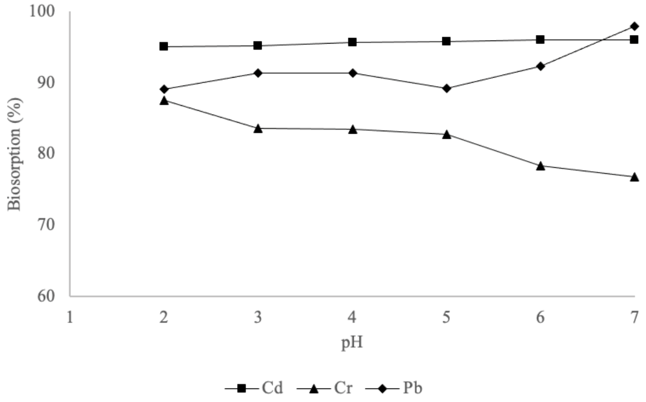


Fig. 5. Effect of solution pH on Cd(II), Cr(VI), and Pb(II) biosorption on CMPNL.

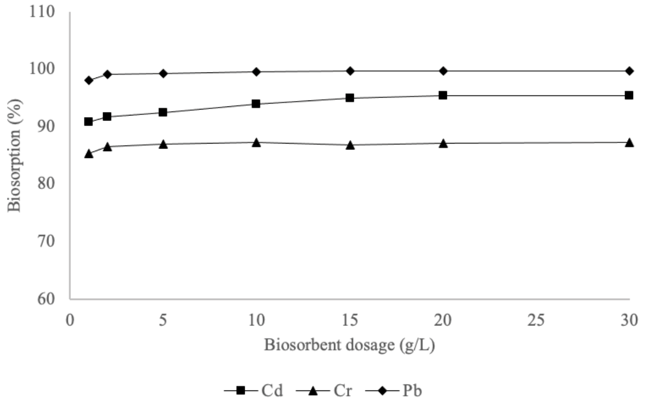


Fig. 6. Effect of biosorbent dosage on Cd(II), Cr(VI), and Pb(II) biosorption on CMPNL.

The biosorption of heavy metal ion increased with the increase in biosorbent dosage up to 5 g/L dosage (optimum dosage) after which biosorption process proceeded with a steady rate. Adsorbents have pores acting as adsorbing sites and with increase in their amount (adsorbent dosage) effective surface area available for adsorption increases [25].

3.3. Isotherms applied

3.3.1. Langmuir isothermal model

Langmuir model deals with sorption of pollutants in the form of monolayer on adsorbent surface having definite number of active sites. The Langmuir isotherm model in linearized form can be given as [26].

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

where C_e (mg/L) is the equilibrium concentration of selected metals, q_e (mg/g) is biosorbed metal's amount per unit mass of biosorbent, K_L (L/mg) is Langmuir constant and q_m (mg/g) is the maximum biosorption capacity.

The C_e/q_e against C_e plot of selected metals is shown in Fig. 7 while the numerical values of the Langmuir model parameters are presented in Table 2.

3.3.2. Freundlich isotherm model

Freundlich isotherm model is an empirical equation applied to adsorption processes taking place on adsorbent associated with multilayer heterogeneous surfaces. The linearized form of Freundlich isotherm can be given as follows [27]:

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

where C_e (mg/L) is the equilibrium concentration of Cd(II), Cr(VI), and Pb(II), q_e (mg/g) is the quantity of metals adsorbed per unit mass of CMPNL at equilibrium, n is Freundlich constant and K_F is the biosorption capability. n and K_F can be calculated from the plot of $\ln q_e$ vs. $\ln C_e$ as shown in Fig. 8 and their numerical values are given in Table 2.

The data of biosorption of Cd(II), Cr(VI), and Pb(II) on CMPNL were accommodated well by Langmuir as compared with Freundlich model, with maximum biosorption capacity (q_m) of 107.526, 208.3, and 172.413 mg/g, respectively, for Cd(II), Cr(VI), and Pb(II).

3.4. Kinetic study of heavy metals biosorption

Intra-particle diffusion, pseudo-first, and second order models have been applied to evaluate the experimental kinetics data.

3.4.1. Pseudo-first order model

The linear form of pseudo-first order kinetics model can be given as follows [28]:

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

where q_t (mg/g) and q_e (mg/g) are the quantity of Cd(II), Cr(VI), and Pb(II) biosorbed at time t and at equilibrium, respectively. K_1 (1/min) is the rate constant of pseudo-first order model. The value of K_1 and q_e can be calculated from the slope and intercept of plots as shown in Fig. 9. The numerical values of the mentioned parameters are given in Table 3.

3.4.2. Pseudo-second order model

The linear form of second order kinetic model can be given as follows [29]:

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

In Eq. (6), K_2 (g/mg/min) is the rate constant for pseudo-second order model. The values of q_e and K_2 were calculated from the slope and intercept of t/q_t vs. time graph as shown in Fig. 10 while their numerical values are given in

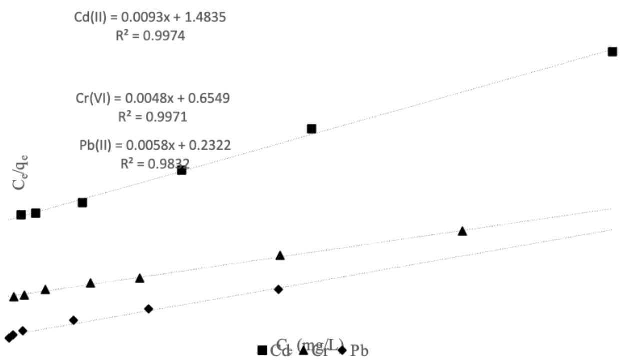


Fig. 7. Langmuir plot of Cd(II), Cr(VI), and Pb(II) biosorption on CMPNL.

Table 2
Langmuir and Freundlich constants of Cd(II), Cr(VI), and Pb(II) biosorption on prepared adsorbent

Isothermal models	Parameters	Cations		
		Cd(II)	Cr(VI)	Pb(II)
Langmuir	$q_{\max}$ (mg/g)	107.526	208.3	172.413
	K_L (L/mg)	0.006	0.007	0.024
	R^2	0.9974	0.9971	0.983
Freundlich	K_F (mg/g)	1,137	1.960	6.755
	n	1.294	1.211	1.702
	R^2	0.9838	0.9931	0.959

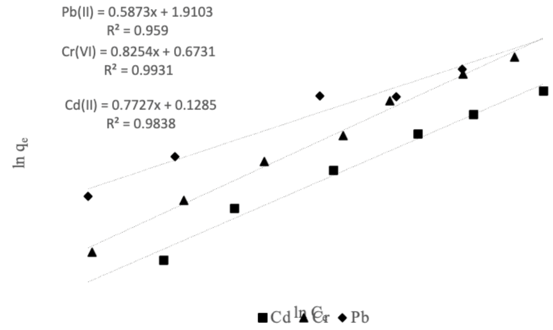


Fig. 8. Freundlich plot of Cd(II), Cr(VI), and Pb(II) biosorption on CMPNL.

Table 3. Based on R^2 value, it was concluded that pseudo-second order kinetic model is best to explain the under study process.

3.4.3. Intra-particle diffusion model

The Intra-particle diffusion model was applied in order to determine the rate controlling step of Cd(II), Cr(VI), and Pb(II) biosorption on CMPNL. The linearized form of this model is given as follows [30]:

$$q_t = K_{\text{diff}} t^{1/2} + C \tag{7}$$

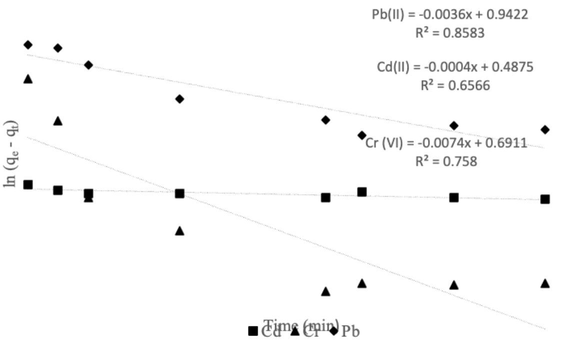


Fig. 9. Pseudo-first order kinetic plots of Cd(II), Cr(VI), and Pb(II) biosorption on CMPNL.

Table 3
Kinetic parameters of selected metals biosorption on CMPNL

Kinetic model	Parameters	Metal		
		Cd(II)	Cr(VI)	Pb(II)
Pseudo-first order	K_1 (1/min)	0.0004	0.0074	0.0036
	q_e (mg/g)	1.628	1.995	2.565
	R^2	0.758	0.6566	0.8583
Pseudo-second order	K_2 (g/mg min)	7.246	0.110	0.074
	q_e (mg/g)	19.230	19.193	16.583
	R^2	1	0.982	0.9922
Intra-particle diffusion	K_{diff} (mg/g min$^{1/2}$)	0.0141	0.3418	0.1601
	C	19.092	22.931	18.692
	R^2	0.7702	0.8387	0.9598

where q_t is the quantity of Cd(II), Cr(VI), and Pb(II) biosorbed at time t, K_{diff} (mg/g min$^{1/2}$) represents a constant while C (mg/g) is intercept relating to the thickness of boundary while their values are presented in Table 3. As the linear portions of the curves (Fig. 11) for all the selected metals do not pass through the origin; thus indicating that intra-particle diffusion is not the only rate-controlling step for the biosorption of these metals on prepared biosorbent [30].

3.5. Thermodynamic studies

To obtain the numerical values of thermodynamic parameters, adsorption experiments were carried out at 20°C, 30°C, 40°C, and 50°C and standard enthalpy ($\Delta H°$), standard entropy ($\Delta S°$), and Gibbs free energy ($\Delta G°$) values were enumerated using following equations [31]:

$$\log\left(\frac{q_e}{C_e}\right) = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{8}$$

where q_e/C_e = biosorption coefficient, $\Delta H°$ and $\Delta S°$ are the change in enthalpy and entropy, respectively, for biosorption of Cd(II), Cr(VI), and Pb(II) on CMPNL and R is the universal gas constant (8.314 J/mol) and T is temperature (K) [25].

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

Metal	$\Delta H°$ (kJ/mol)	$\Delta S°$ (kJ/mol)	$\Delta G°$ (kJ/mol)			
			298 K	303 K	313 K	323 K
Cd(II)	–16.369	57.722	–16.896	–17.473	–18.051	–18.628
Cr(VI)	–9.544	34.424	–10.076	–10.421	–10.765	–11.094
Pb(II)	–25.268	86.008	–25.175	–26.035	–26.895	–27.755

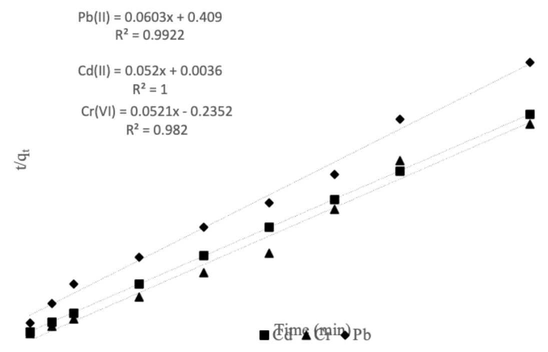


Fig. 10. Pseudo-second order kinetic plots of Cd(II), Cr(VI), and Pb(II) biosorption on CMPNL.

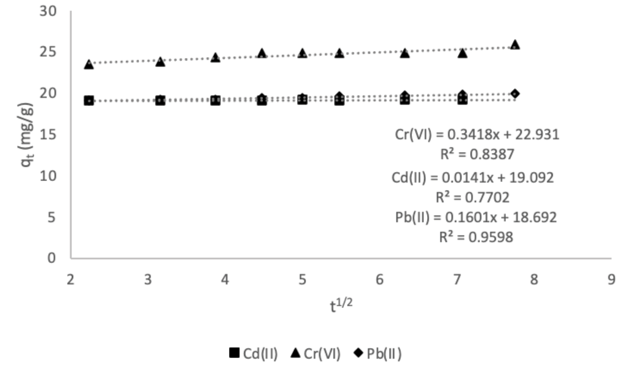


Fig. 11. Intra-particle diffusion plot of Cd(II), Cr(VI), and Pb(II) biosorption on CMPNL.

By plotting $\log q_e/C_e$ against $1/T$ as shown in Fig. 12, the values of $\Delta H°$ and $\Delta S°$ were calculated from the slope and intercept of the plot (Van't Hoff's plot). The values of $\Delta H°$ were negative while that of $\Delta S°$ were positive pointing towards the exothermic and spontaneous nature of biosorption process. The values of standard Gibbs free energy ($\Delta G°$) at 20°C, 30°C, 40°C, and 50°C were calculated using the following equation [32]:

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

The negative values of $\Delta G°$ corresponds to the favorable nature of Cd(II), Cr(VI) and Pb(II) biosorption on CMPNL at different temperatures as shown in Table 4.

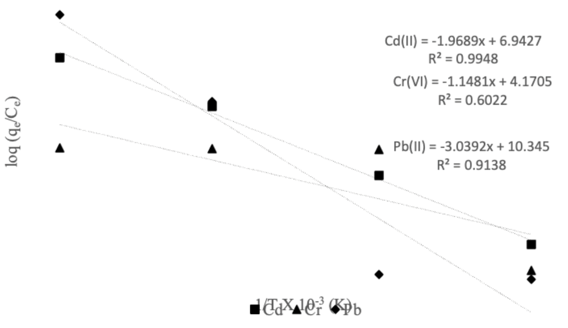


Fig. 12. Van't Hoff's plot of Cd(II), Cr(VI), and Pb(II) biosorption on CMPNL.

3.6. Regeneration of biosorbent

The prepared biosorbent was regenerated six times using NaOH, methanol, and distilled water treatments. The biosorption capacities dropped from 92% to 46% with slight variations among the selected metals.

4. Conclusion

From the results of the study, it can be concluded that CMPNL, as a low-cost biosorbent can be effectively used for the removal of Cd(II), Cr(VI), and Pb(II) from aqueous media. The equilibrium data fitted well to Langmuir isotherm model rather than Freundlich model. The kinetics data followed pseudo-second order model rather than pseudo-first order kinetics models with high R^2 value. The values of $\Delta H°$ were negative for Cd(II), Cr(VI), and Pb(II) and that of $\Delta S°$ were positive pointing towards the exothermic and spontaneous nature of the process. The negative values of $\Delta G°$ showed the favorable nature of Cd(II), Cr(VI), and Pb(II) metal ions biosorption on CMPNL at high temperatures.

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