#### **ORIGINAL ARTICLE**



# Optimization study of adsorption parameters for removal of Cr(VI) using *Magnolia* leaf biomass by response surface methodology

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## Abstract

The removal of chromium (Cr) using waste biomass is one of the most important issues throughout the world. In the present study, *Magnolia* leaf, a forest waste, is employed as novel and available adsorbent to abate Cr(VI) from simulated solution through batch study. The effects of operating variables on biosorption were analyzed using a multi-step response surface methodology (RSM). The optimum biosorption conditions were determined at the initial Cr(VI) concentration of 40.0 mg L<sup>-1</sup>, pH of 2.0, contact time 45.0 min and dose of 0.5 g. At optimum conditions, the biosorption capacity of *Magnolia* leaf for Cr(VI) was found to be 3.96 mg g<sup>-1</sup> that reflects the removal of 98.8%. The obtained data matched with the pseudo-second-order rate ( $R^2 = 0.987$ ) expression and fitted the Langmuir isotherm ( $R^2 = 0.999$ ) very well. The thermodynamic parameters such as  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  for the Cr(VI) biosorption were calculated at six different temperatures. The surface characteristics and the existence of chromium of the biomass, before and after biosorption, were studied through scanning electron micrographs–energy-dispersive X-ray spectroscopy (SEM–EDX) and Fourier transform infrared (FTIR) analysis. The present results indicate that *Magnolia* leaf is a suitable low-cost bio-material to remove Cr(VI) from aqueous solutions.

Keywords Magnolia leaf · Biosorption · Cr(VI) removal · Isotherm · Optimization · Response surface methodology

## Abbreviations

ANOVA	Analysis of variance
BBD	Box-Behnken design
EDTA	Ethylene diamine tetra acetic acid
FTIR	Fourier transform infrared
MLP	Magnolia leaf powder
RSM	Response surface methodology
SEM	Scanning electron micrographs

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# Introduction

Heavy metals are considered as a significant public health problem because they are non-biodegradable and have a persistent nature (Sahan and Ozturk 2014). They can be accumulated through the food chain even at low concentrations, leading to a threat to aquatic life as well as to animal and plant life and human health. The presence of heavy metals in drinking water sources and in edible agricultural crops is harmful to human. It is well known that heavy metals are toxic as they damage nerves, liver and bones by blocking functional groups of vital enzymes (Gholami et al. 2006). Chromium (Cr) is one of the most abundant metals present in groundwater contaminants to hazardous level particularly in waste sites. It is widely used in modern industries such as leather tanning, electroplating, cement, steel, paint, dyes and textiles. The two most common and widely available oxidation states of chromium are Cr(III) and Cr(VI). Among the available oxidation states, Cr(VI) is considered to be potentially carcinogenic to humans and is reported to be bioaccumulated into flora and fauna, creating ecological problems (Koyuncu 2012). Compared to its trivalent counterpart, hexavalent chromium forms chromate  $(CrO_4^{2-})$  or hydrogen chromate (HCrO<sub>4</sub><sup>-</sup>) that is more soluble at different pH. Because of the negative charge, chromate adsorption on aquifer minerals is limited, making it more mobile in subsurface soils and aquifers (Swarnakar et al. 2011). Toxicity of Cr(VI) is due to the negative charge on hexavalent chromium ion complexes which easily pass through cellular membrane using sulphate ionic channels and subsequently transform into various harmful intermediates (Wang and Shen 1995). The maximum permissible limit for chromium discharge onto land surfaces is 0.1 mg L<sup>-1</sup> and is 0.05 mg L<sup>-1</sup> for drinking water (WHO 1993). Therefore, proper removal techniques have to be implemented to overcome this heavy metal contamination, especially Cr(VI).

Conventional separation techniques, for instance electrochemical precipitation, slow sand filtration, reverse osmosis, ion-exchange and solvent extraction have many drawbacks, for example: the high cost, possible production of secondary toxic compounds and the generation of sludge leading to high disposal costs (Jing et al. 2011; Albadarin et al. 2012). Adsorption separation is one of the most economically favorable and technically feasible methods for the decontamination of Cr(VI) from aqueous solution. Adsorptive removal studies of Cr(VI) have focused on the application of activated carbons because of their extended surface area, micro/mesoporous structure and significant adsorption capacity (Rai et al. 2016; Parlayici et al. 2015; Wang et al. 2010). However, owing to the high cost and difficult procurement of activated carbon (Lyu et al. 2017; Li et al. 2017), efforts are being directed towards finding efficient and lowcost adsorbent materials.

Among the variety of low-cost adsorbents for chromium removal, there has been an increase in the use of biomasses (biosorbents) because they are readily available and ecofriendly. Previous literature highlighted that Cr(VI) can be removed by using spent cyanobacterial biomass (Mona et al. 2011), cationic surfactant-modified spent mushroom (Jing et al. 2011), immobilized cyanobacterium biomass (Kiran et al. 2007), etc. However, nowadays much attention has been focused towards effective use of low-cost and easily available agricultural waste for decontamination of chromium from aqueous medium. Previous researchers used different agricultural waste such as hazelnut cactus leaf (Mohanty et al. 2005), eucalyptus bark (Sarin and Pant 2006), sorghum root (Choudhary et al. 2015), coffee husk (Ahalya et al. 2010), sunflower head (Jain et al. 2010), beet pulp (Cimino et al. 2000), etc., for the removal of Cr(VI). However, still there is very limited research to use plant leaf as an effective biosorbent for removal of Cr(VI) from aqueous medium.

In assessing the effect of operational variables on biosorptive removal of Cr(VI), the use of an adequate experimental design is particularly important. The traditional method involves changing one independent operating variable while maintaining others at a fixed level is an extremely time-consuming operation process. To overcome this difficulty, response surface methodology (RSM) has been introduced. It helps to optimize the effective variables with a minimum number of experiments, as well as to analyze the interaction between the variables. Recently, RSM has drawn much attention to the investigators to obtain the optimal conditions for the biosorptive removal of Cr(VI) (Das et al. 2013a; Kumar and Phanikumar 2013; Ahmady-Asbchin et al. 2015; Samuel et al. 2015).

Therefore, the present study is aimed to achieve the maximum biosorptive removal of Cr(VI) by *Magnolia* leaf powder (MLP), for which kinetic parameters and adsorption capacity of the biosorbent are studied, along with response surface methodology (RSM). Box–Behnken model in RSM is used to analyze the effectiveness of the system under four operating variables. The entire experimental data are statistically justified by using analysis of variance (ANOVA) and lack-of-fit to evaluate the significance of the model. Results obtained from this study are presented and discussed.

## Materials and methods

#### **Reagents and apparatus**

Chemicals of analytical grade were procured from M/S, Merck India Ltd., and used for the current investigation without further purification. All reagents and standards were prepared using double distilled water. Stock solution (100 mg L<sup>-1</sup>) of Cr(VI) was prepared by dissolving 0.2829 g  $K_2Cr_2O_7$  in 1000 mL double distilled water and the required Cr(VI) concentrations were prepared by serial dilution of stock solution on daily basis. All borosilicate glassware were cleaned by being soaked in 15% HNO<sub>3</sub> and rinsed with double distilled water. Before mixing the biosorbent (MLP), the pH of each Cr(VI) solution was adjusted to the required value by adding 0.1 (M) NaOH or HCl solution whenever necessary.

#### Adsorbent collection and preparation

*Magnolia* is a large genus of about 210 flowering plant species in the subfamily Magnolioideae of the family Magnoliaceae. It is named after French botanist Pierre Magnol. *Magnolia* is an ancient genus. Having evolved before bees appeared, the flowers developed to encourage pollination by beetles. To avoid damage from pollinating beetles, the carpals of *Magnolia* flowers are extremely tough. Fossilized specimens of *Magnolia acuminate* have been found dating to 20 million years ago and of plants identifiably belonging to the Magnoliaceae dating to 95 million years ago. Another primitive aspect of *Magnolias* is their lack of distinct sepals or petals. *Magnolia* possess undifferentiated flower parts for which the term "tepals" was coined (Johnstone 1955).

For the present investigation, the *Magnolias* leaves were collected from the hilly region of Darjeeling, West Bengal (India). The collected leaves were washed thrice with double distilled water to remove the adhering dirt and water-soluble impurities; and then dried until the leaves become crisp. The dried leaves are ground to a fine powder and rewashed until the washings were free of color and turbidity. The *Magnolia* leaf powder (MLP) is re-dried and sieved to 300 µm prior to use as biosorbent without any physical and chemical treatment.

#### Adsorbent characterization

The *Magnolia* leaf powder (MLP) was characterized by scanning electron micrograph–energy-dispersive X-ray study (HITACHI S530), Fourier transform infrared spectroscopy (FTIR) study (BRUKER, Tensor 27) and double beam UV–Vis spectrophotometry (Perkin Elmer, Lamda 35).

#### **Batch adsorption procedure**

In batch biosorption study, the effects of initial Cr(VI) concentration (20.0–50.0 mg  $L^{-1}$ ), pH of the solution (2.0–8.0), dose of biosorbent (0.3–0.6 g) and contact time (15.0–60.0 min) were evaluated at room temperature  $(313 \pm 1 \text{ K})$  and constant stirring rate of 500 rpm. The 50 mL solution of Cr(VI) was taken in each Erlenmeyer flask separately. After pH adjustment, a known quantity of dried MLP was added and the Cr(VI)-bearing suspensions was kept under magnetic stirring until equilibrium was reached. After shaking, the suspension was allowed to settle down and filtered (0.65 micron). The filtrate was collected and subjected to Cr(VI) estimation using 1,5 diphenyl carbazide method followed by spectrophotometric determination at a wavelength of 540 nm. The Cr(VI) concentrations before and after biosorption were recorded, and the amount of Cr(VI) adsorbed per unit MLP (mg  $g^{-1}$  biosorbent) was calculated according to mass balance on the Cr(VI) concentration using Eq. (1):

$$q_{\rm e} = \frac{(C_{\rm i} - C_{\rm e}) \times V}{m},\tag{1}$$

where  $C_i$  and  $C_e$  (mg L<sup>-1</sup>) are the initial and equilibrium concentration of Cr(VI), respectively. *V* is the volume of solution (L) and *m* is the mass of the biosorbent (g) used.

The percentage removal (biosorption) of Cr(VI) was also calculated as:

Removal (%) = 
$$\frac{(C_{\rm i} - C_{\rm e}) \times 100}{C_{\rm i}}$$
. (2)

## **Regeneration study**

The entire regeneration of the spent adsorbent was studied by using 0.1 M HNO<sub>3</sub> followed by double distilled water and finally dried in hot air over at 60 °C for 24 h.

### **Box–Behnken design**

RSM is extensively used in the field of adsorption or removal for its multi-factor experiments and to find out a common point among various operating variables in most favorable or un-favorable conditions of the process. To optimize the process variables, the most successful Box–Behnken design (BBD) in RSM is performed for this adsorption study.

In BBD maximum number of experiment required according to  $N = k^2 + k + c_p$ , where (k) is the factor number and  $c_p$  is the replicate number of the central point. Moreover, BBD is a spherical, rotating design, and looks like a cubic shape and consists of central point and the middle points of the edges. This particular design is very efficient in terms of required run numbers which are either rotable or nearly rotable. This design is usually fitting to the second-order polynomial model as depicted in the following Eq (3):

$$Y_i = b_0 + \sum_{i=1}^n b_i x_i + \left(\sum_{i=1}^n b_{ii} x_i\right)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} x_i x_j,$$
(3)

where  $Y_i$  is the predicted response;  $b_0$  is the intercept;  $b_i$ ,  $b_{ij}$ , and  $b_{ii}$  are coefficients of the linear effect, double interactions;  $x_i$  and  $x_i$ , are the independent variables or factors.

## **Desorption study**

For the desorption study, the exhausted (Cr-loaded) MLP biomass was contacted with 50 mL of different desorbing solutions of 0.1 (M) EDTA, HCl and HNO<sub>3</sub>. The mixture was stirred at 500 rpm for 60 min, filtered and analyzed. The percentage of desorption of Cr(VI) was calculated from the following Eq. (4):

$$% Desorption = \frac{\text{amount of } Cr(VI) \text{ desorbed to the desorption medium}}{\text{amount of } Cr(VI) \text{ adsorbed onto the biosorbent medium}} \times 100.$$
(4)



Fig. 1 Effect of pH on the biosorption of Cr(VI) (experimental conditions: initial chromium concentration,  $30.0 \text{ mg L}^{-1}$ ; dose, 0.5 g; contact time, 30.0 min)

# **Results and discussion**

## **Batch operation**

#### Effect of pH

The pH of the solution is one of the most critical parameters in the adsorption process, which affects surface charge of the adsorbent material and the degree of ionization and specification of adsorbate. The effect of pH on the removal efficiency of Cr(VI) was studied at different pH values ranging from 2.0 to 8.0. The results are presented in Fig. 1. It was observed that a significant decrease in the Cr(VI) removal occurred when the pH of the solutions changed from 2.0 to 8.0. The maximum biosorption of Cr(VI) was obtained at pH 2.0. So pH 2.0 was selected as optimum pH for Cr(VI) biosorption onto MLP biomass. Almost similar acidic pHdependent chromium removal was reported by Mondal et al. (2017). From the stability diagram, it was evident that the most prevalent form of Cr(VI) in aqueous solution was acid chromate (HCrO<sub>4</sub><sup>-</sup>), chromate (CrO<sub>4</sub><sup>2-</sup>), dichromate  $(Cr_2O_7^{2-})$  and other oxyanions of Cr. However, dominant form of Cr(VI) at initial pH of 2.0 is HCrO<sub>4</sub><sup>-</sup> which is converted to other forms like  $CrO_4^{2-}$  and  $Cr_2O_7^{2-}$  with increasing in pH (Donmez and Aksu 2002). The decrease in Cr(VI) removal efficiency at higher pH (Kazemi et al. 2018) might be due to the competition between  $OH^-$  and  $CrO_4^{2-}$  ions, where the former being the dominant wins the race.

Again the FTIR spectral analysis indicates the presence of –OH functional group onto biomass surface. This –OH group is protonated at lower pH and thereby facilitate the interaction of  $HCrO_4^-$  ion to the surface of the biosorbent that results in higher uptake of Cr(VI). With decrease in acidity of the solution, the functional groups on the biosorbent surface become de-protonated resulting in an increase of negative charge density on the MLP surface. Consequently, there is weakening of electrostatic force between adsorbate and adsorbent which ultimately led to the lowering of biosorption capacity. Almost similar observations have been reported by the earlier researchers for biosorption of Cr(VI) by various biosorbents such as almond shell at pH 1.0 (Demirbas et al. 2004), coconut shell at pH 2.5 (Alaerts et al. 1989), coconut shell and fiber at pH 2.0 (Mohan et al. 2005), hazelnut shell at pH 2.0 and 1.0 (Cimino et al. 2000; Kobya 2004).

#### Effect of initial Cr(VI) concentration

The rate of adsorption is a function of the initial concentration of the adsorbate, which makes it an important factor to be considered for effective adsorption. The effect of different initial Cr(VI) concentration on biosorption of Cr(VI) onto MLP biomass is presented in Fig. 2. The percentage removal of Cr(VI) was decreased with increasing the initial Cr(VI) concentration. It seems that all biosorbents have a limited number of active sites and at a certain concentration the active sites become saturated (Ahmady-Asbchin et al. 2015; Parlayici et al. 2015). However, the biosorption capacity at equilibrium was increased with increase in initial Cr(VI) concentration. It is possible that the initial concentration provides the necessary driving force to overcome the mass transfer resistance of Cr(VI) ion between the aqueous and the solid phase (Ang et al. 2013; Samuel et al. 2015). The increase in the initial Cr(VI) concentration also enhances the interaction between the Cr(VI) ion in the aqueous phase and the biomass surface; resulted in higher uptake of Cr(VI) for the given amount of biomass.



**Fig. 2** Effect of initial chromium concentration on the biosorption of Cr(VI) (experimental conditions: dose, 0.5 g; contact time, 30.0 min; pH, 2.0)



**Fig. 3** Effect of biosorbent dose on the biosorption of Cr(VI) (experimental conditions: initial chromium concentration, 40.0 mg  $L^{-1}$ ; contact time, 30.0 min; pH, 2.0)

#### Effect of biosorbent dose

In this study, different biosorbent dosages were selected ranging from 0.3 to 0.6 g while the Cr(VI) concentration was fixed at 40.0 mg  $L^{-1}$  and pH 2.0. The results are presented in Fig. 3. The results revealed that percentage of Cr(VI) removal was increased with increase in biosorbent dose. Such a trend is mostly attributed to an increase in the biosorptive surface area and the availability of more active binding sites on the surface of biomass (Albadarin et al. 2012; Das et al. 2014; Roy et al. 2015). However, the equilibrium biosorption capacity showed an opposite trend. As the biosorbent dosage was increased from 0.3 to 0.6 g, the biosorption capacity reduced from 5.2 to 3.28 mg  $g^{-1}$ . This may be due to the decrease in total surface area available for Cr(VI) ion resulting from overlapping or aggregation of biosorption sites. Thus with increasing biosorbent mass, the amount of Cr(VI) adsorbed onto unit mass of biosorbent gets reduced, thus causing a decrease in  $q_e$  value with increasing MLP mass concentration. Furthermore, maximum Cr(VI) removal (98.2%) was recorded by 0.5 g MLP biomass and further increase in biosorbent dose did not significantly change the biosorption yield. This is probably due to the non-availability of active sites on the biosorbent and establishment of equilibrium between the Cr(VI) on the biosorbent and in the solution (Das et al. 2013b). The results agree with the observation by Chaudhuri and Azizan (2012) for removal of Cr(VI) by using agricultural waste-based activated carbon.

#### Effect of contact time

The uptake of Cr(VI) as a function of contact time is shown in Fig. 4. As illustrated in Fig. 4, biosorption of Cr(VI) was



**Fig. 4** Effect of contact time on the biosorption of Cr(VI) (experimental conditions: initial chromium concentration, 40.0 mg  $L^{-1}$ ; dose, 0.5 g; pH, 2.0)

increased with rise in contact time up to 45.0 min. Further increase in contact time did not increase the Cr(VI) biosorption process and the equilibrium was reached after 45.0 min. The fast biosorption rate at the initial stage may be explained by abundant availability in the number of active binding sites on the biosorbent surface (Das et al. 2013a; Roy et al. 2014). The biosorption occurs rapidly and normally, was controlled by the diffusion process from the bulk to the surface. In the later stage, the biosorption becomes an attachment-controlled process due to less availability of biosorption sites. Similar findings for Cr(VI) biosorption onto other biosorbents have been reported in the earlier literature (Samuel et al. 2015; Ahmady-Asbchin et al. 2015).

#### FTIR study

The FTIR spectrum was carried out as a qualitative analysis to determine the main functional groups that are involved in the biosorption process. The FTIR spectrum of the unloaded MLP (Fig. 5a) shows the complex nature of the biomass. The broad and intense peak at 3321 cm<sup>-1</sup> indicate the presence of free or hydrogen bonded -OH groups (alcohol, phenols, and carboxylic acids) as in cellulose, pectin and lignin on the surface of the biosorbent (Choudhary et al. 2015). The O-H stretching vibration occurs within a broad range of frequencies indicating the presence of "free" hydroxyl groups and bonded -OH bands of carboxylic acids. The peak observed at 2916 and 2849 cm<sup>-1</sup> can be attributed to the C–H stretching vibrations of aliphatic acids (Gnanasambandam and Proctor 2008). On the other hand, peak observed at 1726  $\rm cm^{-1}$ corresponds to the stretching vibrations of C=O bond due to the non-ionic carboxylic groups, and may be assigned to carboxylic acid or their esters (Yun et al. 2001).



Fig. 5 a FTIR of MLP biomass before Cr(VI) biosorption. b FTIR of MLP biomass after Cr(VI) biosorption

Asymmetric stretching vibration of ionic carboxylic groups appears at 1612 and 1610 cm<sup>-1</sup>. The peak of 1366 and 1424 cm<sup>-1</sup> can be attributed to symmetric stretching of  $-COO^-$  of pectin (Yun et al. 2001). The strong C–O band noted at 1026 cm<sup>-1</sup> is probable due to  $-OCH_3$  which also confirms the presence of lignin structure in MLP. It is clear from the FTIR spectra that carboxylic and hydroxyl groups

are present in abundance. The biosorption of Cr(VI) onto MLP biomass may be likely due to electrostatic attraction between these groups and the Cr(VI) ions. However, after biosorption of Cr(VI) under optimization conditions of batch operation; a new peak at 2307 cm<sup>-1</sup> was recorded, which corresponds to the triple bond ( $-C\equiv C-$ ) stretching frequency and it clearly indicates that the Cr(VI) ions



Fig. 6 a SEM micrograph of MLP before Cr(VI) adsorption, b EDX micrograph of MLP before Cr(VI) adsorption

definitely interact with the biosorbent (Fig. 5b). Moreover, there is a minor shift of the peak in the lower frequency from 1026 to 1027 cm<sup>-1</sup> which possibly due to the binding of C–O group along with hexavalent chromium (Srividya and Mohanty 2009).

#### SEM-EDX study

The surface morphology of the unloaded MLP biomass was examined by SEM–EDX (Fig. 6a), which clearly reveals a flocked and porous surface texture. As seen in Fig. 6a, the biosorbent had some heterogeneity in its structure capable of Cr(VI) ions uptake and Fig. 6b also indicates the absence of chromium before adsorption. However, after biosorption, the surface of biomass has flattened (Fig. 7a) in comparison to raw sample due to the heavy impregnation of Cr(VI) onto the surface of the MLP and Fig. 7b clearly demonstrates the presence of chromium on the surface of MLP. Moreover, before Cr(VI) loading stomatal aperture was wide. But, after Cr(VI) loading stomatal aperture was filled with the chromium and subsequently the neat chromium concentration was reduced



Fig. 7 a SEM micrograph of MLP after Cr(VI) adsorption, b EDX micrograph of MLP after Cr(VI) adsorption

in the solution phase and this phenomenon again directly proved by EDX study. Almost similar surface morphology of lignin was reported by Albadarin et al. (2011) after biosorption of Cr(VI).

#### Adsorption isotherms and kinetics study

An adsorption (biosorption) isotherm represents the equilibrium relationship between the adsorbate concentration in the liquid phase and that on the adsorbents surface at a given condition. A number of isotherms have been developed to describe equilibrium relationships. In the present study, the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) models were used to describe the equilibrium isotherms. The summarization of the adsorption isotherm models is shown Table 1.

From Table 1, it is observed that the Langmuir isotherm showed good fit to the experimental equilibrium data than the Freundlich, Temkin and D–R isotherm equation for Cr(VI) biosorption according to the values of  $R^2$ . It is also seen from Table 1 that the Langmuir maximum biosorption capacity  $q_{\text{max}}$  (mg g<sup>-1</sup>) is 12.3 and the equilibrium constant  $K_{\text{L}}$  (L mg<sup>-1</sup>) is 0.008. The separation factor ( $R_{\text{L}}$ ) values are 0.861, 0.805, 0.755 and 0.712 while initial Cr(VI) concentrations are 20.0, 30.0, 40.0 and 50.0 mg L<sup>-1</sup>, respectively. All the  $R_{\text{L}}$  values were found to be less than one and greater than zero indicating the favorable biosorption of Cr(VI) by MLP. The Freundlich constant  $K_{\rm F}$  indicates the adsorption capacity of the biosorbent and the value of  $K_{\rm F}$  is 10.2 mg g<sup>-1</sup>. Furthermore, the value of 'n' at equilibrium is 1.96. The value of n lies in between 1 and 10 also represents a favorable biosorption. From Temkin constant,  $B_{\rm T}$  related to adsorption binding energy for Cr(VI) is found to be 3.13 J mol<sup>-1</sup> (<20 J mol<sup>-1</sup>), clearly denying to follow the ion-exchange and chemisorption mechanism. In addition, D–R isotherm shows the value of the adsorption energy (*E*) of 5.86 kJ mol<sup>-1</sup>. The estimated value of *E* (<8 kJ/mol) has been indicated towards the physisorption process (Baig et al. 2010; Das et al. 2013b; Roy et al. 2015).

The pseudo-first-order and pseudo-second-order kinetic models were tested to investigate the rate of biosorption of Cr(VI) by MLP (Baig et al. 2010; Chattoraj et al. 2014). The linearized form of adsorption kinetics and their constants are presented in Table 2. From the table, it is confirmed that the Cr(VI) biosorption followed the pseudo-second-order reaction. It is also clear that the pseudo-second-order kinetic model showed excellent linearity with high correlation coefficient ( $R^2$  = 0.987) at 40.0 mg L<sup>-1</sup> Cr(VI) concentration in comparison to the first-order kinetic model. Furthermore, the calculated  $q_e$  value also agrees with the experimental value (3.97 mg g<sup>-1</sup>) in the case of pseudo-second-order kinetic model.

Adsorption isotherms	Equations	Parameters (unit)	Values	$R^2$
Langmuir isotherm	$\frac{1}{1} = \frac{1}{1} + \frac{1}{1}$	$q_{\rm max} ({\rm mg \ g^{-1}})$	12.3	0.999
	$q_{\rm e} = q_{\rm max} \kappa_{\rm L} c_{\rm e} = q_{\rm max}$	$K_{\rm L}$ (L mg <sup>-1</sup> )	0.008	
Freundlich isotherm	$\log q_{\rm e} = \log K_{\rm F} + \frac{1}{n} \log C_{\rm e}$	$K_{\rm F} ({\rm mg \ g^{-1}})$	10.2	0.992
	n	n	1.96	
Temkin isotherm	$q_{\rm e} = B_{\rm T}(\ln A_{\rm T} + \ln C_{\rm e})$	$A_{\rm T}$ (L mg <sup>-1</sup> )	11.13	0.981
		$B_{\rm T}$ (J mol <sup>-1</sup> )	3.13	
D–R isotherm	$\ln q_{\rm e} = \ln q_{\rm max} - \frac{1}{2E^2} \times \left[ RT \ln \left( 1 + \frac{1}{C_{\rm e}} \right) \right]^2$	$q_{\rm max}  ({ m mg g}^{-1})$	11.5	0.939
		$E (\mathrm{kJ}\mathrm{mol}^{-1})$	5.86	

 $q_{\text{max}}$  is the maximum biosorption capacity;  $K_{\text{L}}$ ,  $K_{\text{F}}$ ,  $A_{\text{T}}$  and  $B_{\text{T}}$  are different biosorption constants; *n* is the heterogeneity factor; *E* is the mean free energy of biosorption per mole of the adsorbate; *T* is the temperature (K), and *R* is the ideal gas constant (8.3145 J mol<sup>-1</sup> K<sup>-1</sup>

Kinetic models	Equations	Parameters (unit)	Values	$R^2$
Pseudo-first-order	$\ln(q_{\rm e} - q_{\rm t}) = \ln q_{\rm e} - k_1 t$	$q_{\rm e} ({\rm mg \ g^{-1}})$	3.59	0.885
		$k_1 (\min^{-1})$	0.235	
Pseudo-second-order	$\frac{t}{a} = \frac{1}{k_a a^2} + \frac{t}{a}$	$q_{\rm e} ({\rm mg \ g^{-1}})$	4.01	0.987
	$q_1  r_2 q_e  q_e$	$k_2 (\mathrm{g} \mathrm{mg}^{-1} \mathrm{min}^{-1})$	0.798	

 $q_t$  is the biosorption capacity at time t;  $k_1$  and  $k_2$  are the first-order and second-order rate constant, respectively

 Table 2
 Kinetic parameters for

 biosorption of Cr(VI) by MLP

Table 1Isotherm data forbiosorption of Cr(VI) by MLP

Table 3 Thermodynamic parameters for biosorption of Cr(VI) by MLP

Thermodynamic parameters	Equations	Values (kJ mol <sup>-1</sup> )
Standard free energy	$\Delta G^0 = -RT \ln K_{\rm C}$	·
313		-12.54
318		-13.10
323		-13.72
328		-14.43
333		-15.28
338		-13.92
Standard enthalpy change	$\ln K_{\rm C} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$	-12.46
Standard entropy change	K KI	0.080

 $K_{\rm C}$  is the equilibrium constant; T and R are as defined in previous equation

 Table 4 Experimental ranges and levels of independent variables

 employed in the BBD

Variables	Units	Notations	Level of vari- ables	
			Low	High
рН		A	2.0	8.0
Initial Cr(VI) concentration	$mg L^{-1}$	В	20.0	50.0
Biosorbent dose	g	С	0.3	0.6
Contact time	min	D	15.0	60.0

#### Thermodynamic study

In order to describe thermodynamic properties for the biosorption of Cr(VI) by MLP, enthalpy change ( $\Delta H^{\circ}$ ), Gibbs free energy change ( $\Delta G^{\circ}$ ) and entropy change ( $\Delta S^{\circ}$ ) were calculated by using equations shown in Table 3.

From Table 3, it is clear that the reaction is spontaneous in nature as rG° values are negative at all the temperature studied. Increase in value of rG° with increase in temperature suggests that lower temperature makes the biosorption easier. Again negative rH° value implies that the biosorption is exothermic in nature. The type of biosorption can be explained in terms of the magnitude of rH°. The enthalpy or the heat of adsorption ranging from 2.1 to 20.9 kJ mol<sup>-1</sup> corresponds to physical adsorption, whereas ranging from 20.9 to 418 kJ mol<sup>-1</sup> is regarded as chemical adsorption. Therefore, the rH° value (12.46 kJ mol<sup>-1</sup>) confirms that the biosorption process of Cr(VI) by MLP occurred due to physisorption. Furthermore, the positive rS° value also corresponds to an increase in the degree of freedom of the adsorbed species during the biosorption process (Baig et al. 2010; Das et al. 2014; Roy et al. 2014).

## Box-Behnken design

The use of RSM has been accentuated for developing, improving and optimizing the complex processes and to evaluate the magnitude of various operational variables (Chowdhury et al. 2013; Roy et al. 2014). For this experimental design of optimization of Cr(VI) biosorption on MLP was done by applying RSM through four levels Box–Behnken design (BBD). The experimental range of the operational variables (viz. pH, initial Cr(VI) concentration, biosorbent dose and contact time) with their units and notation is given in Table 4. According to this design, a total of 29 experiments were employed to the BBD matrix and the most successful quadratic model was selected, via stepwise regression mode, to continue the progress.

#### Development of regression model equations and ANOVA

The adequacy and significance of the selected model can be further evaluated using the analysis of variance (ANOVA). The evidences were Fisher variation ratio (F value), probability value (p value), lack of fit, coefficient of determination *R*-squared  $(R_d^2)$ , adjusted *R*-squared  $(R_{Adj}^2)$ , predicted *R*-squared  $\left(R_{\text{Pred}}^2\right)$  and adequate precision. Adequate precision is a signal-to-noise ratio, which compares the range of the predicted values at the design points to the average prediction error. The ratios greater than 4 indicate adequate model discrimination.  $R_{Adi}^2$  and the  $R_{Pred}^2$  are measurements of the amount of variation around the mean and newly explained data, respectively. The p value represents the degree of significance of each variable while F value is a statistically valid measure of how well the factors describe the variation in the data about its mean (Kumar and Phanikumar 2013; Chattoraj et al. 2014; Sadhukhan et al. 2014; Roy et al. 2015).

The quadratic model was validated by ANOVA (Tables 5, 6) which provided evidences such as high *F* values (73.71; 875.35), very low *p* value (<0.0001), non-significant lack of fit (5.76; 2.80), as well as high values for coefficient of *R*-squared ( $R_d^2 = 0.961$ ; 0.996), adjusted *R*-squared ( $R_{Adj}^2 = 0.948$ ; 0.995), predicted *R*-squared ( $R_{Pred}^2 = 0.859$ ; 0.986) and the adequate precision (35.09; 117.52) (Table 7) for both the responses (removal and biosorption capacity). Moreover, Fig. 8a, b shows the actual values versus predicted values of the Cr(VI) biosorption for batch study, which indicates an excellent agreement between the actual and predicted values. As observed, the validity (significance and adequacy) of the model was confirmed by the reasonable evidence.

The empirical relationships relating the removal and equilibrium biosorption capacity of Cr(VI) on MLP biomass, to the tested variables expressed in terms of unitless regression coefficient by the selected quadratic model are given by the following equations:

Table 5ANOVA for percentageremoval of Cr(VI) by MLP

Source	Sum of squares	df	Mean square	F value	p value, Prob > $F$	
Model	801.90	7	114.56	73.71	< 0.0001	Significant
А	51.01	1	51.01	32.82	< 0.0001	
В	22.82	1	22.82	14.69	0.0010	
С	359.68	1	359.68	231.43	< 0.0001	
D	164.03	1	164.03	105.54	< 0.0001	
$\mathbf{B}^2$	5.43	1	5.43	3.50	0.0755	
$C^2$	43.98	1	43.98	28.30	< 0.0001	
$D^2$	135.02	1	135.02	86.87	< 0.0001	
Residual	32.64	21	1.55			
Lack of fit	31.36	17	1.84	5.76	0.0510	Not significant
Pure error	1.28	4	0.32			
Cor total	834.54	28				

Table 6ANOVA forbiosorption capacity of Cr(VI)by MLP

Source	Sum of squares	df	Mean square	F value	p value, Prob > $F$	
Model	16.23	6	2.70	875.35	< 0.0001	Significant
A	0.05	1	0.05	16.33	0.0005	
В	7.58	1	7.58	2452.41	< 0.0001	
С	3.26	1	3.26	1054.28	< 0.0001	
D	0.26	1	0.26	84.59	< 0.0001	
$B^2$	0.02	1	0.02	5.73	0.0256	
$D^2$	0.23	1	0.23	73.94	< 0.0001	
Residual	0.07	22	0.00			
Lack of fit	0.06	18	0.00	2.80	0.1644	Not significant
Pure error	0.01	4	0.00			
Cor total	16.29	28				

Table 7 Model summary statistics

Parameters	Removal	Biosorption capacity
Std. Dev.	1.25	0.06
Mean	94.80	3.57
CV. %	1.32	1.56
PRESS	117.65	0.24
R-squared	0.961	0.996
Adj R-squared	0.948	0.995
Pred R-squared	0.859	0.986
Adeq precision	35.09	117.52

Removal (%) = 
$$+95.11 - 2.86A - 2.41B + 10.27C$$
  
+  $6.46D - 1.92B^2 - 5.59C^2 - 9.54D^2$ , (5)

Biosorption capacity (mg g<sup>-1</sup>) = 
$$+3.78 - 0.09A$$
  
+  $1.37B - 0.96C + 0.26D - 0.11B^2 - 0.39D^2$ , (6)

where A (pH), B (initial Cr(VI) concentration), C (biosorbent dose) and D (contact time) are in coded factors.

A regression analysis of the model equation (Tables 5, 6) shows that the main as well as the square effects of the operational variables were highly significant. p value greater than 0.1000 indicate the model term was not significant.

#### **Optimization using desirability functions**

In the numerical optimization, we choose the desired goal for each factor and response from the menu. The possible goals are: maximize, minimize, target, within range, none (for response only) and set to an exact value (factors only). The goals are combined into an overall desirability function. The program seeks to maximize this function (Roy et al. 2014; Sadhukhan et al. 2014). The optimum biosorption conditions were determined at the pH of 2.0, initial Cr(VI) concentration of 40.0 mg L<sup>-1</sup>, dose of 0.5 g and contact time 45.0 min. Under optimized conditions, the biosorption capacity of *Magnolia* leaf for Cr(VI) was found to be 3.96 mg g<sup>-1</sup> that reflects the removal of 98.8%





Desirability = 0.995

Fig. 9 Ramp plot for optimization procedure



Fig.8 a Plot of actual versus predicted response for the removal of Cr(VI). b Plot of actual versus predicted response for the uptake of Cr(VI)

at maximum desirability value of 0.995 (Fig. 9). The optimized result obtained from BBD coincides well with experimental values, suggesting that the MLP may be an effective biosorbent for the removal of Cr(VI) from water.

## **Desorption study**

The adsorption technology will be economical if exhausted adsorbent could be regenerated (Mondal et al. 2015). Desorption experiment showed the regeneration of MLP

Fig. 10 Desorption study of Cr(VI) loaded MLP biomass with different solutions

biomass and recovery of Cr(VI). To perform the desorption study, the exhausted MLP biomass was collected after operating the biosorption experiment at optimal conditions. The Cr-loaded MLP was washed gently with double distilled water to remove any unadsorbed Cr(VI) and dried prior to use for desorption study. The desorption percentage of Cr(VI) from MLP using different desorbing solutions is presented in Fig. 10. It is evident from the figure that maximum 83% of Cr(VI) can be desorbed with 0.1 (M) HNO<sub>3</sub>. And the weight loss of the biosorbent was insignificant at the end of desorption. Thus a remarkable amount of Cr(VI) is being desorbed, which shows that the MLP can be effectively

reused after desorption. The regenerated adsorbent was further used for three consecutive cycles. The third cycle results demonstrated that the adsorbent only removes 62%Cr(VI) which showed 21% reduction in efficiency after third cycle (figure not provided). The efficiency of spent adsorbent gradually reduced, this is possibly due to the inactivation of the active functional groups which are mainly involved for binding of Cr(VI) from aqueous solution. The study agrees well with the earlier reports (Anayurt et al. 2009; Samuel et al. 2015).

# Conclusions

From the present research it has been found that the maximum removal of Cr(VI) was 98.8% with biosorption capacity of *Magnolia* leaf was 3.96 mg  $g^{-1}$ . The high F values, very low p value, non-significant lack of fit, as well as high values for  $R^2$  and the adequate precision, indicated the adequacy and significance of the response surface quadratic model developed by BBD. The study on equilibrium biosorption of batch operation revealed that Langmuir isotherm model gave the best fit to experimental data. The nature of biosorption of Cr(VI) by MLP was physisorption as inferred from the D-R isotherm model. The FTIR analysis shows that -COOH, -OH and -OCH<sub>3</sub> groups present on the surface of the MLP biomass and these groups are supposed to be responsible for binding of Cr(VI). Moreover, the entire biosorption is pseudo-second-order, exothermic and spontaneous in nature. The optimized result of BBD, as well as the experimental values, revealed that the MLP was an effective and economically feasible biosorbent. Overall, it can be concluded that the application of statistical model is an effective approach for optimization, modeling and designing the Cr(VI) biosorption process.

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## **Compliance with ethical standards**

**Conflict of interest** All the authors declared that they have no conflict of interest to publish this paper.

# References

Ahalya N, Kanamadi RD, Ramachandra TV (2010) Removal of hexavalent chromium using coffee husk. Int J Environ Pollut 43((1/2/3)):106–116

- Ahmady-Asbchin S, Safari M, Varposhti M (2015) Biosorption optimization of Cr(VI) using response surface methodology and thermodynamics modeling onto *Azolla filiculoides*. Sep Sci Technol 50(4):554–563
- Alaerts GJ, Jitjaturant V, Kelderman P (1989) Use of coconut shell based activated carbon for chromium(VI) removal. Water Sci Technol 21(12):1701–1704
- Albadarin AB, Mangwandi C, Al-Muhtaseb AH, Walker GM, Allen SJ, Ahmad MNM (2012) Kinetic and thermodynamics of chromium ions adsorption onto low-cost dolomite adsorbent. Chem Eng J 179:193–202
- Albadarina AB, Al-Muhtaseb AH, Al-laqtah NA, Walker GM, Allen SJ, Ahmad MNM (2011) Biosorption of toxic chromium from aqueous phase by lignin: mechanism, effect of other metal ions and salts. Chem Eng J 169(1–3):20–30
- Anayurt RA, Sari A, Tuzen M (2009) Equilibrium, thermodynamic and kinetic studies on biosorption of Pb(II) and Cd(II) from aqueous solution by macrofungus (*Lactarius scrobiculatus*) biomass. Chem Eng J 151(1–3):255–261
- Ang XW, Sethu VS, Andresen JM, Sivakumar M (2013) Copper(II) ion removal from aqueous solutions using biosorption technology: thermodynamic and SEM–EDX studies. Clean Techn Environ Policy 15(2):401–407
- Baig JA, Kazi TG, Shah AQ, Kandhro GA, Afridi HI, Khan S, Kolachi NF (2010) Biosorption studies on powder of stem of Acacia nilotica: removal of arsenic from surface water. J Hazard Mater 178(1–3):941–948
- Chattoraj S, Mondal NK, Das B, Roy P, Sadhukhan B (2014) Biosorption of carbaryl from aqueous solution onto *Pistia stratiotes* biomass. Appl Water Sci 4(1):79–88
- Chaudhuri M, Azizan NKB (2012) Adsorptive removal of chromium(VI) from aqueous solution by an agricultural waste– based activated carbon. Water Air Soil Pollut 223(4):1765–1771
- Choudhary S, Goyal V, Singh S (2015) Removal of copper(II) and chromium(VI) from aqueous solution using sorghum roots (S. bicolor): a kinetic and thermodynamic study. Clean Techn Environ Policy 17(4):1039–1051
- Chowdhury S, Chakraborty S, Saha PD (2013) Response surface optimization of a dynamic dye adsorption process: a case study of crystal violet adsorption onto NaOH-modified rice husk. Environ Sci Pollut Res 20(3):1698–1705
- Cimino G, Passerini A, Toscano G (2000) Removal of toxic cations and Cr(VI) from aqueous solution by hazelnut shell. Water Res 34(11):2955–2962
- Das B, Mondal NK, Roy P, Chattaraj S (2013a) Equilibrium, kinetic and thermodynamic study on chromium(VI) removal from aqueous solution using *Pistia stratiotes* biomass. Chem Sci Trans 2(1):85–104
- Das B, Mondal NK, Roy P, Chattoraj S (2013b) Application of response surface methodology for hexavalent chromium adsorption onto alluvial soil of Indian origin. Int J Environ Pollut Solut 1(2):72–87
- Das B, Mondal NK, Bhaumik R, Roy P (2014) Insight into adsorption equilibrium, kinetics and thermodynamics of lead onto alluvial soil. Int J Environ Sci Technol 11(4):1101–1114
- Demirbas E, Kobya M, Senturk E, Ozklan T (2004) Adsorption kinetics for the removal of chromium(VI) from aqueous solutions on the activated carbons prepared from agricultural wastes. Water SA 30(4):533–540
- Donmez G, Aksu Z (2002) Removal of chromium(VI) from saline wastewaters by *Dunaliella* species. Process Biochem 38(5):751–762
- Gholami F, Mahvi AH, Omrani GA, Nazmara S, Ghasri A (2006) Removal of chromium(VI) from aqueous solution by Ulmus leaves. Iran J Environ Health Sci Eng 3(2):97–102

- Gnanasambandam R, Proctor A (2008) Determination of pectin degree of esterification by diffuse reflectance fourier transform infrared spectroscopy. Food Chem 68(3):327–332
- Jain M, Garg VK, Kadirvelu K (2010) Equilibrium and kinetic studies for sequestration of Cr(VI) from simulated wastewater using sunflower waste biomass. J Hazard Mater 171(1–3):328–334
- Jing X, Cao Y, Zhang X, Wang D, Wu X, Xu H (2011) Biosorption of Cr(VI) from simulated wastewater using a cationic surfactant modified spent mushroom. Desalination 269(1–3):120–127
- Johnstone GH (1955) Asiatic Magnolias in cultivation, 1st edn. The Royal Horticultural Society, London
- Kazemi MO, Jahanshahi M, Peyravi M (2018) Hexavalent chromium removal by multilayer membrane assisted by photocatalytic couple nanoparticle from both permeate and retentate. J Hazard Mater. https://doi.org/10.1016/j.jhazmat.2017.09.059
- Kiran B, Kaushik A, Kaushik CP (2007) Response surface methodological approach for optimizing removal of Cr(VI) from aqueous solution using immobilized cyanobacterium. Chem Eng J 126(2–3):147–153
- Kobya M (2004) Removal of Cr(VI) from aqueous solutions by adsorption onto hazelnut shell activated carbon: kinetic and equilibrium studies. Bioresour Technol 91(3):317–321
- Koyuncu M (2012) Adsorption of Cr(VI) from textile waste water by using natural bentonite. IIOABJ 3(3):1–4
- Kumar MPS, Phanikumar BR (2013) Response surface modelling of Cr<sup>6+</sup> adsorption from aqueous solution by neem bark powder: Box–Behnken experimental approach. Environ Sci Pollut Res 20(3):1327–1343
- Li H, Dong X, da Silva E, DeOliveira LM, Chen Y, Ma LQ (2017) Mechanism of metal sorption by biochars: Biochar characteristics and modifications. Chemosphere 178:466–478
- Lyu H, Tang J, Huang Y, Gai L, Zeng EY, Liber K, Goug Y (2017) Removal of hexavalent chromium from aqueous solutions by a novel biochar supported nanoscale iron sulfide composite. Chem Eng J 322:516–524
- Mohan D, Singh KP, Singh VK (2005) Removal of hexavalent chromium from aqueous solution using low-cost activated carbon derived from agricultural waste materials and activated carbon fabric cloth. Ind Eng Chem Res 44(4):1027–1042
- Mohanty K, Jha M, Meikap BC, Biswas MN (2005) Removal of chromium(VI) from dilute aqueous solutions by activated carbon developed from *Terminalia arjuna* nuts activated with zinc chloride. Chem Eng Sci 60(11):3049–3059
- Mona S, Kaushik A, Kaushik CP (2011) Biosorption of chromium(VI) by spent cyanobacterial biomass from a hydrogen fermentor using Box-Behnken model. Int Biodeterior Biodegrad 65(4):656–663
- Mondal NK, Bhaumik R, Datta JK (2015) Removal of fluoride by aluminum impregnated coconut fiber from synthetic fluoride solution and natural water. Alex Eng J 54(4):1273–1284
- Mondal NK, Samanta A, Dutta S, Chattoraj S (2017) Optimization of Cr(VI) biosorption onto *Aspergillus niger* using 3-level

Box-Behnken design: equilibrium, kinetic, thermodynamic and regeneration studies. J Genetic Eng Biotechnol 15:151–160

- Parlayici S, Eskizeybek V, Avcı A, Pehlivan E (2015) Removal of chromium(VI) using activated carbon–supported–functionalized carbon nanotubes. J Nanostruct Chem 5(3):255–263
- Rai MK, Shahi G, Meena V, Meena R, Chakraborty S, Singh RS, Rai BN (2016) Removal of hexavalent Cr(VI) using activated carbon prepared from mango kernel activated with H<sub>3</sub>PO<sub>4</sub>. Resour Effic Technol 2:563–570
- Roy P, Mondal NK, Das K (2014) Modeling of the adsorptive removal of arsenic: a statistical approach. J Environ Chem Eng 2(1):585–597
- Roy P, Dey U, Chattoraj S, Mukhopadhyay D, Mondal NK (2015) Modeling of the adsorptive removal of arsenic(III) using plant biomass: a bioremedial approach. Appl Water Sci. https://doi. org/10.1007/s13201-015-0339-2
- Sadhukhan B, Mondal NK, Chattoraj S (2014) Biosorptive removal of cationic dye from aqueous system: a response surface methodological approach. Clean Techn Environ Policy 16(6):1015–1025
- Sahan T, Ozturk D (2014) Investigation of Pb(II) adsorption onto pumice samples: application of optimization method based on fractional factorial design and response surface methodology. Clean Technol Environ Policy 16(5):819–831
- Samuel MS, Abigail MEA, Ramalingam C (2015) Biosorption of Cr(VI) by *Ceratocystis paradoxa* MSR2 using isotherm modelling, kinetic study and optimization of batch parameters using response surface methodology. PLoS ONE 10(3):e0118999. https ://doi.org/10.1371/journal.pone.0118999
- Sarin V, Pant KK (2006) Removal of chromium from industrial waste by using eucalyptus bark. Bioresour Technol 97(1):15–20
- Srividya K, Mohanty K (2009) Biosorption of hexavalent chromium from aqueous solutions by Catla catla scales: equilibrium and kinetics studies. Chem Eng J 155:666–673
- Swarnakar V, Agrawal N, Tomar R (2011) Sorption of Cr(VI) & As(V) on HDTMA –modified zeolites. Int J Sci Eng Res 2(5):1–9
- Wang YT, Shen H (1995) Bacterial reduction of hexavalent chromium. J Ind Microbiol 14(2):159–163
- Wang XS, Chen LF, Li FY, Chen KL, Wan WY, Tang YJ (2010) Removal of Cr(VI) with wheat–residue derived black carbon: reaction mechanism and adsorption performance. J Hazard Mater 175(1–3):816–822
- WHO (1993) Guidelines for drinking-water quality, 2nd edn. Switzerland, Geneva
- Yun YS, Park D, Park JM, Volesky B (2001) Biosorption of trivalent chromium on the brown seaweed biomass. Environ Sci Technol 35(21):4353–4358

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