Korean J. Chem. Eng., 33(2), 567-575 (2016)
DOI: 10.1007/s11814-015-0165-0

pISSN: 0256-1115
eISSN: 1975-7220

Characterization, isotherm and kinetic study of *Phaseolus vulgaris* husk as an innovative adsorbent for Cr(VI) removal

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(*Received 11 April 2015 • accepted 30 July 2015*)

Abstract–*Phaseolus vulgaris* husk as a novel, very common milling agro waste, showed good performance for mutagenic Cr(VI) removal from chromium enriched aqueous solution. The study involves batch experiments to investigate the effects of influencing parameters, such as pH, temperature, contact time, initial Cr(VI) concentration, and adsorbent dose, on the adsorption process. Results showed a maximum of 99.88% removal of Cr(VI) at pH 1.16, temperature 20 °C and adsorbent dose of 6 g L^{-1}. The adsorption equilibrium data followed the Freundlich model, suggesting a heterogeneous nature of the adsorbent surface and the correlation coefficient for pseudo-second-order kinetic model was found to be very high, showing its applicability during the adsorption process. The maximum Cr(VI) uptake capacity was 3.4317 mg g^{-1}. Thermodynamic parameters like standard free energy change (–7.175 kJ mol^{-1}), enthalpy change (–8.29 kJ mol^{-1}) and entropy change (0.005 kJ mol^{-1} K^{-1}) revealed the spontaneous and exothermic nature of adsorption of Cr(VI) onto *P. vulgaris* husk. Desorption with 1 mol L^{-1} NaOH followed by 1 mol L^{-1} HCl was effective (92.76%) and, hence, it exhibited the possibility of recycling of used husk.

Keywords: Mutagenic Cr(VI), *Phaseolus vulgaris* Husk, Freundlich Isotherm, Correlation Coefficients, Pseudo Second Order, Exothermic

INTRODUCTION

Various pollutants, including heavy metals, are released from a range of natural and anthropogenic activities and enter the food chain through drinking water and crop irrigation, a wall to wall problem, especially in densely populated developing and poor countries. Chromium is a heavy metal widely used in various industries, including chrome plating, wood preservation, leather tanning, pulp production, film and photography, petroleum refining, pigments, catalysis, metal finishing, brass, and electrical and electronic equipment. It is used as a strong oxidizing agent in organic chemistry [1]. Chromium occurs in the environment either in trivalent Cr(III) or hexavalent Cr(VI) form. Among these two species, Cr(VI) is known to be carcinogenic and mutagenic as well as being a strong oxidizing agent causing irritation in plant and animal tissues even in very small quantities [2]. Biological membranes are impermeable to Cr(III), but Cr(VI) can easily penetrate the membrane and may be reduced in the mitochondria, nuclei and cytoplasm to Cr(III), which readily forms insoluble chromium hydroxides at pH 7.5. Cr(III), which may be generated inside the cells, binds to protein and interacts with nucleic acids.

Earlier studies reported a quite large range of chromium concentration in natural waters, ranging from 5.2 to 208,000 mg L^{-1} [3]. Nevertheless, the maximum contaminant level for Cr(VI) in domestic water supplies is less than 0.05 mg L^{-1}, recommended for drinking water by the World Health Organization or the US Environmental Protection Agency [4].

A large number of treatment technologies, as listed in Table 1, with advantages and disadvantages, have been developed for the removal of chromium from the aquatic medium. Chemical reduction and precipitation, ion exchange, electrodialysis, reverse osmosis, solvent extraction, electrochemical precipitation and biosorption have been suggested for the removal of Cr(VI). But these methods are expensive and ineffective, especially when the concentration of heavy metals in the wastewater is low [5]. Biosorption is an emerging technology which involves sorption of dissolved substances by biomaterials. It seems to be an efficient technique for the removal of heavy metal ions, and through this technique recovery and recycling of the adsorbent materials can also be possible along with the distinct benefits of nonproduction of toxic chemical sludge and cost effectiveness [6]. Biosorption of Cr(VI) pollutants has been natural biosorbents (which are mostly cellulose-based materials) are cost effective, relatively abundant and ubiquitous in the environment. The emergence of biosorption made it possible to utilize various biological substances, such as raw rice bran, *Agave lechuguilla* biomass, oak sawdust, coir pith, rice husk, saltbush, exhausted coffee, Turkish coffee, waste tea, walnut shell, nut shell, orange peel [7-13] and many more for removal of Cr(VI) from water and wastewaters. Also, magnetic nanoparticles modified with many biological byproducts, such as, orange peel powder, activated carbon [13-15] have been used for the same.

The present work explores the adsorption process of Cr(VI) by using *Phaseolus vulgaris* (red kidney bean) husk. There is not any experimental data available on the characterization and utilization

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Table 1. Current treatment methods for heavy metal removal from waste water, their advantages and disadvantages

S. No	Method	Advantage	Disadvantage
1	Ultrafiltration	Low driving force Small space requirement High packing density	Problem of membrane fouling Biodegradation of membrane material
2	Nanofiltration	Easy operation, reliable, low energy consumption Can treat inorganic effluent with metal concentration up to 200 mg L^{-1} on a wide range of pH and pressure	Costly Prone to membrane fouling
3	Reverse osmosis	Accounts for more than 20% of world desalination capacity Efficient rejection rate	High power consumption due to high operating pressure (20-100 bar) Prone to membrane fouling
4	Coagulation flocculation	Can treat waste water with metal concentration higher than 1,000 mg L^{-1} Improved sludge settling	High operating cost High chemical consumption and toxic sludge generation
5	Floatation	Can treat inorganic effluent with metal concentration of more than 150 mg L^{-1} Effective for small particle removal Shorter hydraulic retention time, low operation cost	To improve heavy metal removal subsequent treatments are required
6	Electrocoagulation	No chemical required as coagulant Low operating cost Simple and easy operation	Cannot remove pollutant directly High initial investment
7	Electrodialysis	Low energy consumption	Feed water pretreatment required to prevent electrodialysis stack fouling
8	Electroxidation	Uses clean reagent as electron No chemical reagent required Simple equipment, easy operation, brief retention time, can treat a wide range of pollutant	High operating cost High energy consumption Risk of electrode fouling
9	Adsorption	Effective and cheap technique with new sorbents Water can be recycled and reused	Adsorbent progressively deteriorating in capacity as number of cycles increases Spent adsorbent may be considered a hazardous waste

of *P. vulgaris* husk for biosorption of Cr(VI). The biosorption potential of this biomass for Cr(VI) reduction and removal was investigated as a function of initial pH, biosorbent dosage, contact time, initial Cr(VI) concentration and shaking speed. The equilibrium biosorption data were evaluated by Langmuir, Freundlich, D-R and BET isotherm models. The biosorption mechanism was also investigated in terms of thermodynamics and kinetics. The data of kinetic studies were evaluated by Lagergren's pseudo first-order and pseudo second-order kinetic models.

MATERIAL AND METHOD

1. Reagents and Solutions

All the chemicals ($K_2Cr_2O_7$, H_2SO_4, Diphenyl carbazide, NaOH, HCl) were of analytical reagent (AR) grade. A stock solution of 1,000 mg L^{-1} Cr(VI) concentration was prepared by dissolving 2.828 g of $K_2Cr_2O_7$ in 1,000 ml double distilled water. This stock solution was diluted to various working concentrations as per requirement.

2. Biosorbent Preparation

P. vulgaris husk an agro waste was collected from the local market of Varanasi, washed with distilled water, dried at 100 °C for 12 h in an thermostatically controlled oven, crushed, milled and sieved. The sieved adsorbent was thermally treated in double distilled water for removal of interfering colors of the biomass.

3. Determination of Cr(VI) Concentration in Aqueous Solution

The concentration of Cr(VI) ions in aqueous solution was determined spectrophotometrically [16] by measurement of the intense red-violet complex formed after reaction of Cr(VI) and 1,5-diphenylcarbazide in an acidic environment. ELICO double beam SL 210 UV-Vis spectrophotometer was used to obtain measurements of the chromophore complex at its absorbance maximum at 540 nm. The instrument was calibrated with the standard stock solution prepared from potassium dichromate. The concentration of Cr(VI) in an unknown sample was estimated by using the standard calibration curve (concentration vs. absorbance) prepared from ten standard Cr(VI) solution with concentrations ranging from 0.1 to 1.0 mg L^{-1}.

4. Batch Biosorption Studies

Batch mode of adsorption studies was used to determine the adsorption of Cr(VI) on biosorbent. The general method used for

the present study is described as follows: 0.3 g adsorbent was equilibrated with 50 mL of 10 mg L^{-1} Cr(VI) solution in a stoppered Pyrex glass flask at a fixed temperature in a thermostatic shaker bath. The initial pH of the solution was adjusted with 0.1 mol L^{-1} HCl and 0.1 mol L^{-1} NaOH solutions and the stirring speed was fixed at 180 rpm to maintain the adsorbent particles in suspension and well mixed conditions. The adsorbent and solution were separated by filtration through a filter paper. After separation the adsorbents were washed with double distilled water and the clean filtrate was collected in a separate beaker. The amount of Cr(VI) adsorbed on the adsorbent was calculated from the difference between initial Cr(VI) concentration and Cr(VI) concentration in the filtrate. The amount of Cr(VI) adsorbed per unit mass of adsorbent, q_e (mg g^{-1}), was calculated by using the following Eq. (1):

$$q_e = (C_0 - C_e)\frac{V}{M} \quad (1)$$

where q_e is the amount of Cr(VI) adsorbed (mg g^{-1}) at equilibrium, m is the mass of adsorbent (g), V is the volume of adsorbate (L), and C_0 and C_e are the initial and equilibrium liquid-phase concentrations of Cr(VI) in aqueous solution (mg L^{-1}), respectively. The percent Cr(VI) removal signed as R (%) was calculated using the following Eq. (2):

$$R(\%) = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \quad (2)$$

RESULTS AND DISCUSSION

1. BET, SEM, XRD and FTIR Analysis of Biosorbent

Surface area is an intrinsic property of the adsorbent that can provide crucial information about its adsorption capacity. The BET surface area of the adsorbent was found to be 179.1 m^2 g^{-1} with total pore volume of 0.036 cm^3 g^{-1}. The large surface area and greater pore volume of *P. vulgaris* husk showed its applicability for Cr(VI) adsorption. Scanning electron microscopy (SEM) enables the direct observation of the surface microstructures of adsorbent. Fig. 1(a) and 1(b) show the SEM image of *P. vulgaris* husk obtained before and after adsorption of Cr(VI), respectively, at the optimum operating condition with 10000×magnification. Native *P. vulgaris* husk has a shiny, bulky and smooth structure with higher degree of homogeneity. The presence of Cr(VI) ions is clearly indicated in the form of rough, irregular and corroded layer over the surface of the metal loaded *P. vulgaris* husk. The X-ray diffraction (XRD) plot of *P. vulgaris* husk and Cr(VI) loaded *P. vulgaris* husk shown in Fig. 1(c) and 1(d) illustrates the presence of significant amount of amorphous material because of SiO_2 and $CaSiO_3$ [17]. The XRD patterns of the *P. vulgaris* husk before and after biosorption with Cr(VI) indicate that the structure of biosorbent remained unaltered even after Cr(VI) ions biosorption. The XRD analysis was also confirmed by SEM analysis of unloaded and Cr(VI) loaded biosorbent in which only a change in the surface smoothness occurred without any alteration in the surface morphology.

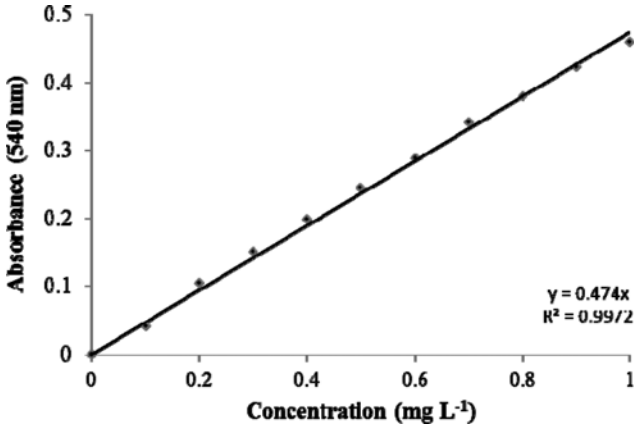

Fig. 1. Standard calibration curve for the spectrophotometric determination of Cr(VI).

Fourier transform infrared (FTIR) spectrum was carried out as a qualitative analysis and results were used to identify functional groups present on the surface of *P. vulgaris* husk that could be responsible for uptake of Cr(VI) ions. The spectrum of the *P. vulgaris*

Table 2. FTIR analysis of *Phaseolus vulgaris* husk before and after adsorption of Cr(VI)

Band position (cm^{-1})			Assignment
Before adsorption	After adsorption	Differences	
3832	3797	+35	Typical -OH stretching
3434	3424	+10	-OH stretching vibration of intra and inter molecular hydrogen bonding
3005	3006	−1	-CH stretching vibration of aliphatic acid
1869	1868	+1	-C=O stretching vibration (-COOH, $COOCH_3$)
1748	1735	+13	-C=O stretching vibration (-COOH, -$COOCH_3$)
1639	1657	−18	-C=O stretching vibration (-COOH, -$COOCH_3$)
1558	1580	−22	-N-H bend (1^0) stretching vibration
1506	1476	+30	-N-H bend (1^0) stretching vibration
1196	1191	+5	-C=O stretching vibration
1155	1152	+3	-C=O stretching vibration
1059	1060	−1	-C-OH stretching vibration
852	854	−2	-CH (para) bonding
610	621	−11	Acetylenic C- H bend

husk was measured within the range of wave number 4,000-400 cm^{-1} and shown in Fig. 1(e) for untreated and Cr(VI) treated *P. vulgaris* husk, respectively. Peak at 3,832 cm^{-1} was due to typical O-H stretching of hydroxyl groups. The broad, strong and intense peak at 3,434 cm^{-1} was assigned to the stretching of O-H group due to intra and intermolecular hydrogen bonding of polymeric compounds, such as alcohols, phenols and carboxylic acids as in pectin, cellulose and lignin. The O-H stretching vibrations occur within a broad range of frequencies, indicating the presence of "free" hydroxyl groups and bonded O-H bands of carboxylic acids. The peak at 3,005 cm^{-1} was due to C-H stretching of aliphatic acids. Peaks observed at 1,869, 1,748 and 1,639 cm^{-1} were the stretching vibration of C=O bond

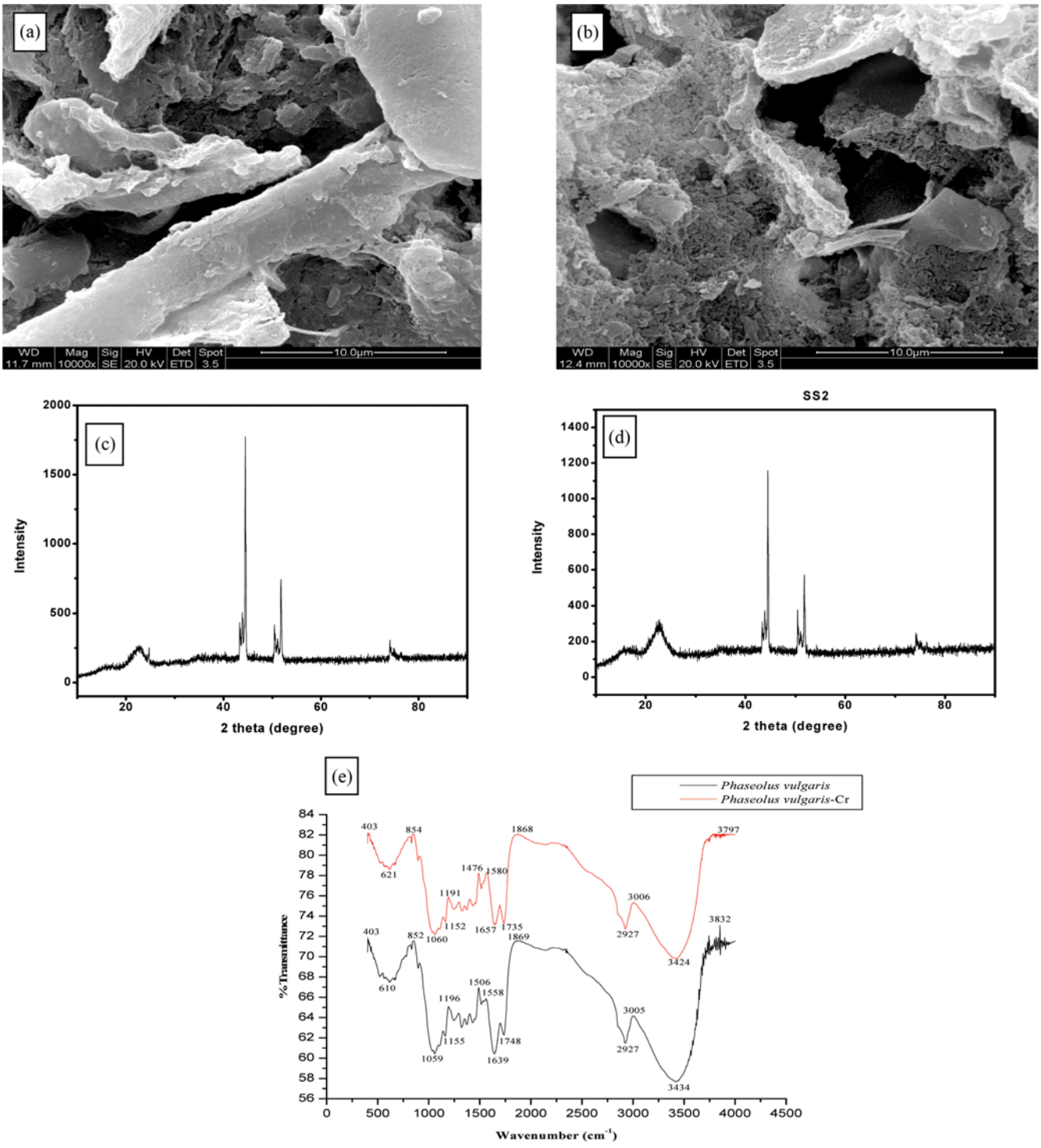

Fig. 2. Characterization of the *Phaseolus vulgaris* husk developed biosorbent (a) SEM micrograph of native (b) SEM micrograph of Cr(VI) loaded (c) XRD plot of native (d) XRD plot of Cr(VI) loaded (e) FTIR spectra of native and Cr(VI) loaded biosorbent.

of non-ionic carboxylic groups (-COOH, -$COOCH_3$) and may be assigned to carboxylic acids or their esters. Peaks at 1,558 and 1,506 cm^{-1} assigned to be N-H bond. Peaks at 1,196 and 1,155 cm^{-1} may be assigned to aliphatic acid group vibration of C=O and stretching formation of -OH of carboxylic acids and phenols, and at 1,059 cm^{-1} can be assigned to stretching vibration of C-OH of alcoholic groups and carboxylic acids. C-H bonds (Para) and an acetylenic C-H bond causes peaks at 852 and 610 cm^{-1}, respectively.

Shift in the peaks from 3,832 to 3,797, 3,434 to 3,424, 3,005 to 3,006, 1,869 to 1,868, 1,748 to 1735, 1639 to 1,657, 1,558 to 1,580, 1,506 to 1,476, 1,196 to 1,191, 1,155 to 1,152, 1,059 to 1060, 852 to 854 and from 610 to 621 cm^{-1} of Cr(VI) sorbed *P. vulgaris* husk shows active involvement of acidic carboxyl, hydroxyl and amine groups in adsorption process (Table 2).

2. Effect of pH

The initial pH of the adsorbate plays a key role in controlling the biosorption of heavy metal ions onto biosorbents. The pH affects the biosorption capacity of biosorbent. The solubility of the metal ions, concentration of the counter ions on the functional groups of the biosorbent surface and the degree of ionization of the biosorbent during reaction are influenced by solution pH [18]. With increased pH from 1.0 to 7.0, percent removal of Cr(VI) decreased 98.59 to 64.16 as shown in Fig. 2. It was observed that the maximum percentage of Cr(VI) removal was at pH 1.16. Higher removal efficiency at low pH is due to presence of oxyanions such as $HCrO_4^-$, CrO_4^- and $Cr_2O_7^{-2}$, in acidic condition. The point of zero charge (pHpzc) of *P. vulgaris* husk was calculated to be 4.8 and at pH< pHpzc the adsorbent indicates the presence of positive functional groups on the surface. These surface positive functional groups exert strong attraction force on oxyanions. Hence, with lower pH, increased Cr(VI) removal occurred [19]. Though, the decrease in Cr(VI) removal with increase in pH may be due to the increase in the hydroxyl ion concentration on the biosorbent surface, which develops a repulsive force between the oxy-anions and the negatively charged surface [20].

3. Effect of Contact Time

The biosorption capacity of *P. vulgaris* husk as a function of time towards different Cr(VI) ion concentrations was studied. The effect of contact time on Cr(VI) ion uptake by the biosorbent was achieved by varying the contact time from 5 to 315 min and initial Cr(VI) concentration from 5 mg L^{-1} to 30 mg L^{-1}. The removal of Cr(VI) ions increased from 78.83 to 99.76% by decreasing concentration of metal from 30 mg L^{-1} to 5 mg L^{-1}. The results shown in Fig. 3 revealed that metal removal from aqueous medium seems to occur in two steps. The first step of biosorption involves rapid uptake of Cr(VI) ions within the first few minutes of contact time followed by the slow and subsequent Cr(VI) ions removal by the biosorbent molecules. It is clear from Fig. 3 that time of equilibrium is the same for all the initial Cr(VI) concentrations. After attainment of equilibrium at around 180 min, the removal efficiency remained almost constant. Initially, the rate of Cr(VI) uptake was higher because all sites on the adsorbent were vacant and Cr(VI) concentration was high, but decrease of sorption sites reduced the uptake rate [21].

4. Effect of Temperature

Temperature is a highly significant parameter in the adsorption processes. To study the effect of temperature variation on biosorption of Cr(VI) ions onto *P. vulgaris* husk, experiments were run at 20, 25, 30, 35 and 40 °C while keeping all other parameters constant. The results of the experiment are in Fig. 4, and the order of adsorption at all the Cr(VI) concentrations was 20 °C>25 °C>30 °C >35 °C>40 °C. It was observed that the percentage of adsorption decreased along with an increase of temperature, the process is exothermic [22].

5. Effect of Adsorbent Dosage

An important parameter for exploring the adsorption process is the dose of the adsorbent. The removal efficiency of *P. vulgaris* husk for a given initial Cr(VI) ion concentration is determined by the concentration of Cr(VI) in adsorbate solution. In the present study, by varying the adsorbent dose from 0.5 to 6 g L^{-1}, we analyzed its effect on metal removal efficiency at a fixed initial Cr(VI) ion concentration of 10 mg L^{-1}. Biosorption of Cr(VI) on surface of *P. vulgaris* husk was increased with increasing biosorbent dosage. Cr(VI) removal efficiency increased from 54.08 to 99.88% as the sorbent dose increased from 0.5 g L^{-1} to 6 g L^{-1} (Fig. 5). Increased percentage of Cr(VI) biosorption with increased biosorbent dose was obvious because with an increase in the dose of the biosorbent, the number of biosorbent molecules also get increased, which

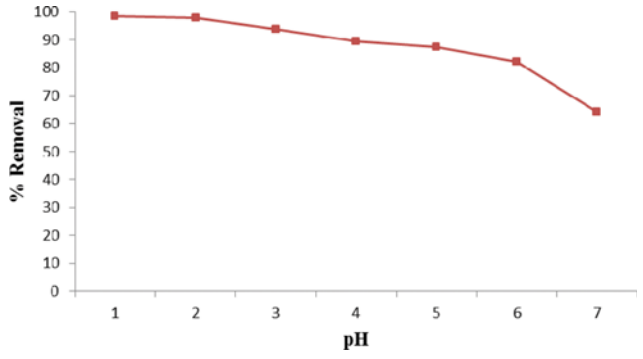

Fig. 3. Percentage adsorption of Cr(VI) ions on *Phaseolus vulgaris* husk from solution of different pH value (initial metal ion concentration: 10 mg L^{-1}, contact time: 180 min, agitation speed: 180 rpm, biosorbent dose: 6 g L^{-1}, temperature: 20 °C).

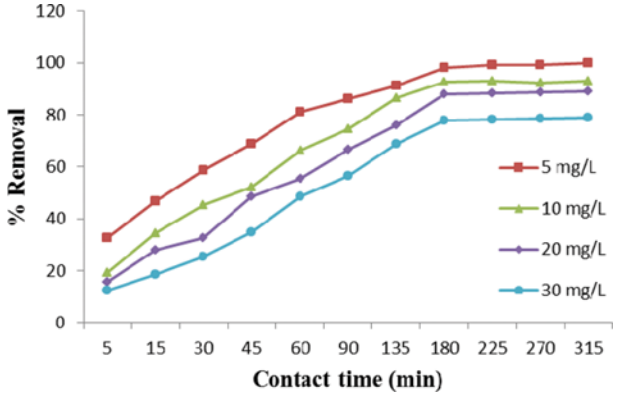

Fig. 4. Percenage removal of Cr(VI) ions from solutions of different concentrations (pH 1.16 shaking speed 180 rpm biosorbnet dose 6 g L^{-1} temperature 20 °C).

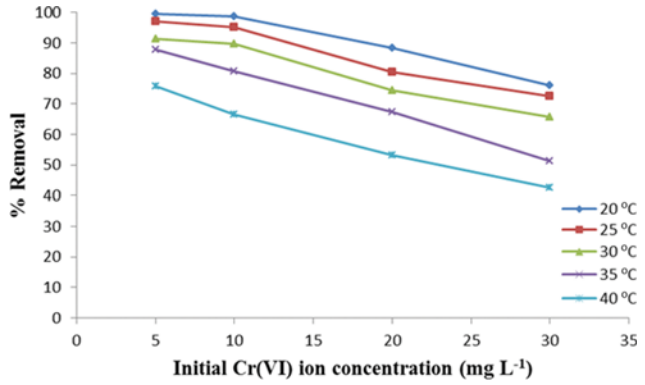

Fig. 5. Effect of temperature on percent adsorption of Cr(VI) ions on *Phaseolus vulgaris* husk at different initial metal ion concentration (pH: 1.16 contact time: 180 min, agitation speed: 180 rpm, biosorbent dose: 6 g L^{-1}).

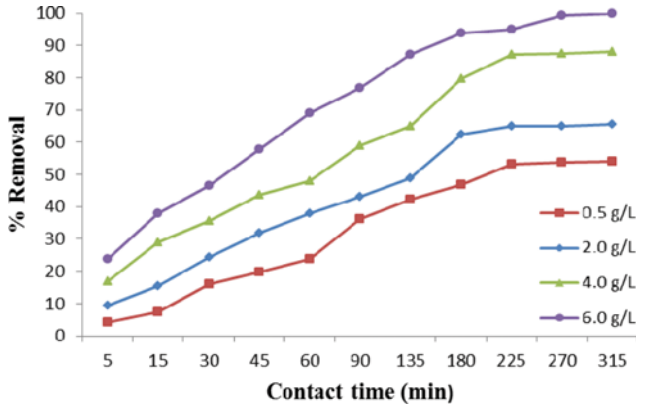

Fig. 6. Effect of contact time on percent adsorption Cr(VI) ions on *Phaseolus vulgaris* husk at different biosorbent doses (pH: 1.16, initial metal ion concentration: 10 mg L^{-1}, shaking speed: 180 rpm, temperature: 20 °C).

facilitates greater availability of vacant active sites for metal biosorption [23].

6. Effect of Shaking Speed

In wastewater treatment process by biosorption technique, it is important to determine the optimal shaking speed because it consumes energy and has a direct effect on biosorption efficiency. In present study, the shaking speed varied from 60 to 300 rpm while all other parameters were kept optimum and constant. Sorption values for Cr(VI) ions were minimum at 60 rpm (43.76%) and increased as the speed of shaking increased up to 180 rpm (Fig. 6). It was the optimum shaking speed at which maximum Cr(VI) removal (99.71%) was observed. With further increase in shaking speed the biosorption efficiency declined. This may have occurred because the high shaking speed provided sufficient additional energy to break newly formed bonds between the biosorbent surface and Cr(VI) ions [24]. A similar study result was reported by Gupta et al. [25].

7. Adsorption Isotherms

The equilibrium adsorption isotherms are fundamental in describing the interactive behavior between adsorbate and biosorbent and are also important in designing of adsorption systems.

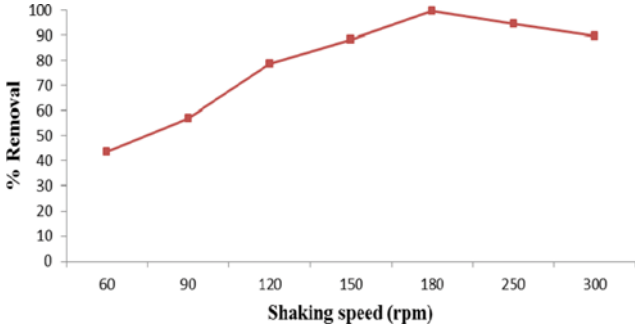

Fig. 7. Effect of shaking speed on percent adsorption of Cr(VI) ions on *Phaseolus vulgaris* husk (pH 1.16, initial metal ion concentration 10 mg L^{-1}, contact time 180 min, temperature 20 °C).

The adsorption equilibrium is established when concentration of adsorbate in the bulk solution is in dynamic balance with that at the biosorbent interface. To examine the relationship between metal adsorbed onto the adsorbent (q_e) and aqueous concentration (C_e) of metals at equilibrium, the Langmuir, Freundlich, Dubinin-Radushkevich (D-R) models are most frequently used [26]. Also Brunauer-Emmer-Teller (BET) isotherm model is used in present study to establish the type of interaction between adsorbate and biosorbent molecule.

The Langmuir isotherm occurs on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions. The basic assumption of the Langmuir model is that forces exerted by chemically unsaturated surface atoms do not extend further than the diameter of one sorbed molecule. The Langmuir model was developed for modeling the adsorption of adsorbate molecules on the energetically uniform surface of the adsorbent molecules [27]. The Langmuir model takes the form of Eqs. (3) and (4);

$$\frac{1}{q_e}=\frac{1}{Q_o}+\frac{1}{bQ_0}\frac{1}{C_e} \tag{3}$$

$$R_L=\frac{1}{1+bC_o} \tag{4}$$

where Q_o and b are Langmuir constants related to the adsorption capacity, and adsorption energy, respectively, C_o is the initial metal ion concentration in mg L^{-1}, C_e is the equilibrium concentration in mg L^{-1}, q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg g^{-1}) and R_L is separation factor. The value of R_L indicates the isotherm model applicability for adsorption of metal ions. According to Jain et al. [28], the isotherm is unfavorable if $R_L>1$, favorable if R_L value is in between 0 to 1 and if R_L value is 1 isotherm is linear while 0 R_L value shows irreversible nature. In present study, R_L value ranges from 0.0007-0.0051 showing favorable isotherm condition.

The Freundlich adsorption isotherm, one of the most widely used mathematical descriptions, gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. Linearized form of Freundlich isotherm Eq. (5) is as:

$$\ln q_e=\ln k_f+\left(\frac{1}{n}\right)\ln C_e \tag{5}$$

Table 3. The isotherms and kinetics constants for Cr(VI) adsorptionon *Phaseolus vulgaris* husk

Langmuir constant			Freundlich constant		
Q_0 (mg g^{-1})	b (L mg^{-1})	R^2	k_F	n	R^2
2.4343	39.0625	0.9024	2.9766	3.3478	0.9575
D-R constant			BET constant		
q_m (mg g^{-1})	k_D	E (kJ mol^{-1})	R^2	q_m (mg g^{-1})	C_{BET} (L mg^{-1})	R^2
2.9901	0.0124	6.3492	0.905	1.9316	101.5099	0.8737
Pseudo-first-order kinetics			Pseudo-second-order kinetics		
k_1 (min^{-1})	q_e (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	R^2
0.1165	4.6441	0.8922	0.0146	2.4545	0.9579

where C_e is the equilibrium concentration in mg L^{-1}, q_e is amount of adsorbate adsorbed per unit mass of adsorbent (mg g^{-1}). 'k_f' is a parameter related to temperature and 'n' is a characteristic constant for the adsorption system under study. The degree of nonlinearity between solution concentration and adsorption is indicated by the value of 'n'. Adsorption is physical process when n>1, if n<1, then it is a chemical process, and n=1 shows the linear nature of the adsorption process [29]. In the Freundlich equation, the n value was found to be 3.3478 (Table 3), which indicates physical adsorption of Cr(VI) ions on to *P. vulgaris* husk. In adsorption study of heavy metal ions on adsorbent surface, the situation of n>1 is very common and this may be because of distribution of surface sites or other factors, which results in a decrease in adsorbate adsorbent interaction with increasing surface density [30]. A value within the range of 1-10 represents good adsorption [31].

The Dubinin-Radushkevich (D-R) adsorption isotherm model is an excellent representation for interpretation of equilibrium conditions for biosorption of compounds on porous solids [32]. The linearized form of the D-R isotherm Eq. (6) is given as:

$$\ln q_e = \ln q_m - k_D \varepsilon^2 \tag{6}$$

where k_D is a coefficient related to adsorption energy, q_m is the maximum adsorption capacity and ε is the Polanyi potential calculated from Eq. (7):

$$\varepsilon = RT\left(1+\frac{1}{C_e}\right) \tag{7}$$

R is the universal gas constant and T is the absolute temperature (K). The constant k_D gives an idea about the mean free energy (E) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated from the D-R isotherm constant k_D by using Eq. (8):

$$E = \frac{1}{\sqrt{2k_D}} \tag{8}$$

The calculated value of E was 6.3492 kJ mol^{-1} confirming the physical nature of Cr(VI) adsorption on *P. vulgaris* husk.

The BET adsorption isotherm model is based on the assumption that on the surface of the adsorbent the adsorbed molecules are arranged in multiple layers. The first layer does not need to be completed before the next layer starts to fill up. Adsorption energy is the same for all the molecules other than the molecules of the first layer, and for the molecules of a given layer the enthalpy of adsorption is the same [33]. The linearized form of BET-isotherm Eq. (9) is given as:

$$\frac{C_e}{q_e(C_s - C_e)} = \frac{1}{q_m C_{BET}} + \frac{(C_{BET}-1)}{q_m C_{BET}}\left(\frac{C_e}{C_s}\right) \tag{9}$$

where q_e is the amount of adsorbed metal ions per unit mass of adsorbents at equilibrium, q_m is the maximum sorption capacity, C_e is the equilibrium concentration of metal ions in solution, C_s is the saturation concentration of the metal ions and C_{BET} is the BET adsorption isotherm related to the energy of surface interaction.

Table 3 summarizes all the correlation coefficients, the R^2 value and the constants obtained from the Langmuir, Freundlich, D-R and BET-isotherm model. On the basis of correlation coefficients (R^2), the Freundlich isotherm model (R^2 0.9575) represents a better fit to the equilibrium data as compared to the Langmuir (R^2 0.9024), D-R (R^2 0.905) and BET (R^2 0.8373) isotherm model. Also, C_e vs q_e plot of various adsorption isotherm models confirm the very close relation between experimental and Freundlich equilibrium data (Fig. 8). Thus, the adsorption of Cr(VI) ions on the surface of *P. vulgaris* husk was heterogeneous with multilayer sorption characteristics. Adsorption capacity of *P. vulgaris* husk and its comparison with various adsorbents used in earlier studies are presented

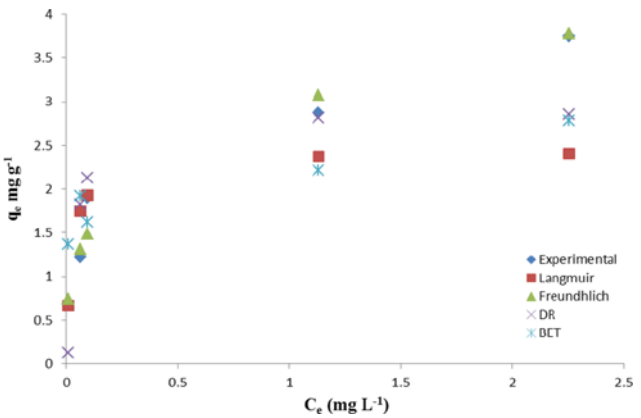

Fig. 8. Adsorption isotherm models for Cr(VI) adsorption from aqueous solution on *Phaseolus vulgaris* husk using batch adsorption process at 20 °C, pH 1.16, contact time 180 min, shaking speed 180 rpm and biosorbent dose of 6 g L^{-1}.

Table 4. Comparison of adsorption capacity of *Phaseolus vulgaris* husk with other previously studied adsorbents

Adsorbents	Temperature (°C)	pH	Model used for adsorption capacity measurement	Adsorption capacity (mg g^{-1})	Reference
Raw rice bran	25	5	Freundlich	0.07	[7]
Agave lechuguilla biomass	10-40	2	Langmuir	2.5-3.4	[8]
Oak sawdust	20	3	Langmuir	1.74	[9]
Coir pith	-	-	Freundlich	0.2	[10]
Rice husk	-	-	Freundlich	0.6	[10]
Saltbush	-	5	Langmuir	0.1	[11]
Exhausted coffee, Turkish coffee, waste tea, nut shell, walnut shell	-	-	Langmuir	1.33-1.63	[12]
Orange peel pith	-	1	Langmuir	1.9	[13]
Phaseolus vulgaris husk	20	1.16	Freundlich	2.98	Present study

in Table 4.

8. Adsorption Kinetics

Adsorption kinetics describes the solute uptake rate, and evidently this rate controls the residence time of adsorbate uptake at the solid-liquid interface. For the study of adsorption kinetics, the contact time was varied from 5 to 315 min with 10 mg L^{-1} concentration of Cr(VI), and at solution pH of 1.16 and the percent removal of Cr(VI) was observed during the course of study. The kinetics of the adsorption data was analyzed by using two kinetic models, Lagergren pseudo-first-order and pseudo-second-order. The linear form of Lagergren pseudo-first-order kinetics is represented by Eq. (10):

$$\log(q_e - q_t) = \log q_e - k_1 \frac{t}{2.303} \tag{10}$$

Ho and McKay pseudo-second-order rate kinetics can be expressed by the following Eq. (11):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{11}$$

where q_t is the amount of Cr(VI) (mg g^{-1} of adsorbent) removed at time t (min), q_e is the amount of Cr(VI) removed at equilibrium, k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the rate constant of adsorption process of pseudo-first-order and pseudo-second-order, respectively. The k_1 and q_e values of pseudo-first-order kinetics were calculated from the slope and intercept of the plot of $\log(q_e - q_t)$ versus t, while in case of pseudo-second-order kinetics the values of k_2 and q_e were obtained from the slope and intercept of the plot of t/q_t versus t as represented in Fig. 9(a) and 9(b). The value of kinetic parameters for both the models are summarized in Table 3. The value of correlation coefficient calculated for pseudo-second-order kinetic model was found to be higher as compared to the pseudo-first-order kinetic model, which supports the assumption that adsorption of Cr(VI) ions on the surface of P. vulgaris husk may be the rate-limiting step involving valence forces through exchange or sharing of electrons between adsorbate and adsorbent [34].

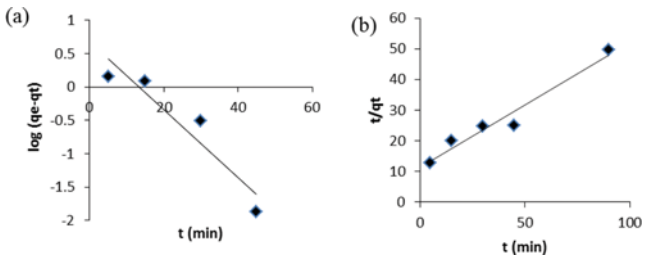

Fig. 9. Kinetic model for adsorption of Cr(VI) ions on *Phaseolus vulgaris* husk (a) pseudo first order, (b) pseudo second order.

9. Thermodynamics for Adsorption

The thermodynamics of adsorption was studied to demonstrate the nature of adsorption of Cr(VI) on *P. vulgaris* husk. Eqs. (12), (13) and (14) have been used to calculate the change in Gibbs free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) for the adsorption process:

$$\Delta G^o = -RT\ln K_c \tag{12}$$

$$\ln K_c = \left(\frac{\Delta S^o}{R}\right) - \left(\frac{\Delta H^o}{RT}\right) \tag{13}$$

$$K_c = \frac{q_e}{C_e} \tag{14}$$

where R is the universal gas constant (kJ mol^{-1} K^{-1}), K_c is the equilibrium constant at temperature T, q_e and C_e are the equilibrium concentrations of adsorbate on the adsorbent and in the solution, respectively. The change in enthalpy (ΔH^o) and entropy (ΔS^o) can be calculated from a plot of $\ln K_c$ vs. 1/T. The degree of spontaneity of the adsorption process was indicated by Gibbs free energy (ΔG^o), and a more negative value of ΔG^o reflects a more energetically favorable adsorption process. As represented in Table 5, the obtained

Table 5. Thermodynamic coefficients for Cr(VI) adsorption on *Phaseolus vulgaris* husk

Temperature (K)	ΔG^o (kJ mol^{-1})	ΔH^o (kJ mol^{-1})	ΔS^o (kJ mol^{-1} K^{-1})
293	−7.175	−8.29	0.005
298	−6.995		
303	−6.789		
308	−6.598		
313	−6.494		

value of ΔG^o in the present study confirms the feasibility of *P. vulgaris* husk as an excellent biosorbent for Cr(VI) biosorption and spontaneity of the biosorption process [35]. In the adsorption process, the values of ΔH^o and ΔS^o were calculated to be −8.29 kJ mol^{-1} and 0.005 kJ mol^{-1} K^{-1}, respectively. The value of ΔH^o was negative, indicating that the sorption process was exothermic [36]. The positive ΔS^o value shows the increased randomness at the solid-liquid interface during the sorption of Cr(VI) onto *P. vulgaris* husk.

DESORPTION STUDY

Desorption of the biosorbent is very important for the regeneration and recovery of the Cr(VI) ions. The 1 mol L^{-1} NaOH followed by 1 mol L^{-1} HCl was used as eluent for desorption of the Cr(VI) ions adsorbed on *P. vulgaris* husk. Within a short period of time 92.76% of the Cr(VI) ions were recovered. After elution of the metal ions, the biosorbent was regenerated by washing with double distilled water and used in the next cycle of adsorption of Cr(VI) ions.

CONCLUSION

SEM and FTIR analysis of *P. vulgaris* husk as biosorbent before and after treatment with the Cr(VI) solution showed significant changes in the surface morphology as well as on the position of various functional groups present on the surface of the biosorbent. These changes were due to binding of the Cr(VI) ions with the biosorbent. On the other hand the XRD plot showed insignificant change in the peaks due to unalteration of the mineral composition of the molecules of biosorbent. Secondly, the process of biosorption of Cr(VI) on biosorbent depends on various parameters including pH, contact time, temperature, biosorbent dose and shaking speed. Maximum biosorption capacity of *P. vulgaris* husk for Cr(VI) was 3.4314 mg g^{-1} detected at pH 1.16. The equilibrium time for attainment of maximum Cr(VI) uptake was 180 min at 20 °C. Finally, the adsorption isotherm data showed good agreement with the Freundlich model, thus supporting multilayer adsorption of the Cr(VI) ions on *P. vulgaris* husk, and the kinetics of the process was pseudo-second-order.

ACKNOWLEDGEMENTS

The Authors are thankful to the Head, Department of Botany, Banaras Hindu University and Department of Chemical Engineering, Indian Institute of Technology (Banaras Hindu University), India for providing all necessary facilities to undertake the work. Authors also thank UGC for financial support.

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