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Chromium (VI) uptake from aqueous solution by adsorption onto timber industry waste

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ABSTRACT

In the present study sawdust, a timber industry waste has been investigated as an adsorbent for the removal of Cr(VI) from synthetic wastewater. Batch mode experiments have been conducted by varying various process parameters including pH, Cr(VI) concentration, adsorbent dose and contact time. Cr(VI) removal was maximum at pH 2. Efficiency of sawdust for Cr(VI) removal from dilute wastewater was 80% at 20 g L^{-1} adsorbent dose. FTIR spectra were recorded to explore number and position of the functional groups available for the binding of Cr(VI) ions onto sawdust. SEMs and EDAX of the adsorbents were recorded to explore the morphology and elemental constitution of the adsorbents. Langmuir, Freundlich and Dubinin–Radushkevich adsorption isotherms were also tested. Pseudo-second order model explains the Cr(VI) kinetic more effectively. Reusability of the adsorbents was examined by desorption in which HCl eluted 79.63% Cr(VI).

Keywords: Sawdust; Chromium; Isotherm; Adsorption; Desorption

1. Introduction

Water pollution by heavy metals is an important economic and environmental issue in numerous parts of the world. These inorganic micro-pollutants are of considerable concern because they are non-biodegradable, highly toxic and have a probable carcinogenic effect [1–3]. Chromium exists in two stable oxidation states, Cr(III) and Cr(VI). The Cr(VI) state is of particular concern because it is hazardous to health [4]. Chromium compounds are widely used by many industries such as leather, tanning, electroplating, metal finishing, paint and pigments, resulting into discharge of large quantity of this element into industrial wastewaters. Waters containing high concentration of chromium can cause serious environmental problems as well as induce toxic and carcinogenic health effects on humans [5]. Therefore, removal of chromium from wastewaters arouses great attention. The permissible limit for Cr(VI) for industrial effluents to be discharge to surface water varies from 0.05 to 0.1 mg L^{-1} in different countries [6]. Hence, chromium containing wastewaters must be treated to reduce Cr(VI) concentration to allowable limits before discharging into environment. Conventional methods applied to remove Cr (VI) from industrial wastewaters include chemical precipitation [7]; activated carbon adsorption [8]; electrochemical precipitation [9]; ion exchange [10]; reverse osmosis [11], etc. These processes apart from being economically expensive have disadvantages such as high reagent and energy requirements, incomplete metal removal, and generation

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of large quantities of toxic sludge, which necessitates careful disposal in further steps [12]. Adsorption has been one of the methods used to remove Cr(VI) from aqueous solutions with relatively low Cr(VI) concentrations. The most widely used adsorbent is activated carbon, but it is not cost-effective. Various agricultural by-products and wastes have been tested for the removal of Cr(VI) from aqueous solutions in the recent past. However, some of the adsorbents do not have good adsorption capacities or require long adsorption equilibrium times. Therefore, there is a need for the development of low cost, easily available materials which could adsorb hexavalent chromium. The studies on the use of sawdust as adsorbent are limited [13]. Timber is widely used for furniture making and the waste sawdust so produced is generally used as cooking fuel due to its zero or negligible cost. The objective of this work was to study the effect of various process parameters on Cr(VI) biosorption by sawdust from synthetic wastewater.

2. Materials and methods

2.1. Preparation of sawdust adsorbent

The sawdust collected from a local saw mill, was dried under sun and impurities were separated manually. The material was grinded and sieved through the sieves of 300 micron size. Then it was boiled with distilled water for 5 h to make it free from colored compounds and filtered. The residual material so obtained was washed several times with distilled water till the filtrate was colourless. This material was dried at 60°C in hot air oven for 24 h and stored in airtight plastic container for further use. The surface morphology and elemental constitutions of the adsorbents were visualized via SEM and EDAX (model Quanta 200 FEG, FEI, Netherlands).

2.2. Preparation of Cr(VI) solution

Synthetic wastewater of Cr(VI) was prepared by dissolving potassium dichromate in double distilled water. Synthetic wastewater containing Cr(VI) solution was diluted with distilled water to obtain the Cr(VI) solutions of desired concentration. pH of the solutions was adjusted using pH meter by 0.01 M NaOH/0.01 M HCl.

2.3. Adsorption experiments

Batch mode experiments were carried out at various pHs (2–7), adsorbent dose (4–20 g L^{-1}) and stirring speed (180 rpm) for a contact time of 180 min. For each experiment, 50 ml Cr(VI) solution of 100 mg L^{-1} concentration was used. After adding desired amount of adsorbent, pH was adjusted and the mixture was agitated on orbital shaker (Scigenics Biotech Orbitek) for pre-determine time intervals. After that the mixture was filtered to separate the adsorbent from solution. The residual chromium concentration in the filtrate was determined by atomic absorption spectrophotometer (Shimadzu 6300, Japan). All experiments were replicated thrice and results were averaged. The removal percentage (R %) of chromium was calculated for each run by following equation:

$$R(\%) = \left[\left(C_i - C_i \right) / C_i \right] \times 100 \tag{1}$$

where C_i and C_e are the initial and residual concentration of chromium in the solution. The adsorption capacity of the adsorbent for each concentration of chromium (VI) at equilibrium was calculated using Eq. (2).

$$q_e(\mathrm{mg \cdot g^{-1}}) = \left[\left(C_i - C_e \right) / M \right] \times V \tag{2}$$

where C_i and C_e are the initial and residual concentration of chromium (mg L^{-1}) in the test solution respectively. V is the volume of solution (L) and M is the mass of adsorbent (in g) used.

3. Results and discussion

3.1. Fourier transform infrared analysis of adsorbents

Fourier transform infrared (FTIR) spectra were used to determine the changes in vibration frequency in the functional groups of the adsorbents due to metal sorption. The spectra of the dry adsorbents were measured within a range of 400–4000 cm^{-1}.

FTIR spectra of native and metal loaded adsorbents are given in Fig. 1a. The FTIR spectrum reveals complex nature of the adsorbent as evident from the presence of several peaks. Table 1 presents absorption peaks and corresponding functional groups on the adsorbent. The adsorption peak around 3614.35 cm^{-1} indicates the existence of free and intermolecular bonded hydroxyl groups which has disappeared in Cr-loaded spectra (Fig. 1b) indicating its participation in metal binding. Peak around 1747.39 cm^{-1} corresponds to C=O stretching attributed to the lignin aromatic groups (Fig 1a) was shifted to 1708.81 cm^{-1} indicating its involving in Cr(VI) adsorption. Peak at 2783.09 cm^{-1} can be assigned to stretching vibration of the C–H which also disappeared in Cr-loaded adsorbent indicating its participation in metal binding. Additional peaks at 532.32 and 451.31 cm^{-1} can be assigned to bending modes of aromatic compounds were shifted to 617.18 cm^{-1} and 487.96 cm^{-1}, respectively.

3.2. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX)

The scanning electron micrographs enable the direct observation of the surface microstructures of a material. The SEM microscopic photos of adsorbent at 1000× magnifications showed irregular cavities in fibrous network which is considered helpful for the accessibility of heavy metals to the adsorbent surface. The micrographs illustrated in Fig. 2a,b clearly indicated the presence of new

Table 1
FT-IR frequencies in native and Cr(VI) loaded adsorbents (in cm^{-1})

Adsorbent	O–H	C–H	C=O	Bending vibrations
SD (native)	3614.35	2783.09	1747.39	532.32, 451.31
SD–Cr(VI)	—	—	1708.81	617.18, 487.96

shiny bulky particles over the surface of metal loaded adsorbent which are absent from the original adsorbent before loading metal ions. It is evident from Fig. 2a,b that the surface morphologies are different of native adsorbent and chromium loaded adsorbent.

EDAX measurements of the samples (with and without metal ion) were also undertaken for qualitative analysis of the elemental constitution of various samples. The EDAX spectrum for native as well as metal ion loaded adsorbent is illustrated in Fig. 2c,d. The samples equilibrated with metal ion solution showed distinct peaks for Cr(VI) metal indicating that the corresponding ion had been sorbed onto the surface of the adsorbent.

3.3. Effect of pH

pH is one of the most important parameters while assessing the adsorption capacity of an adsorbent for metal ions because of its influence on the surface properties of the adsorbent and ionic forms of the chromium in solutions [14–16]. Adsorption experiments were carried out in the pH range of 2–7 while keeping all other parameters constant (chromium concentration = 50 mg L^{-1}; stirring

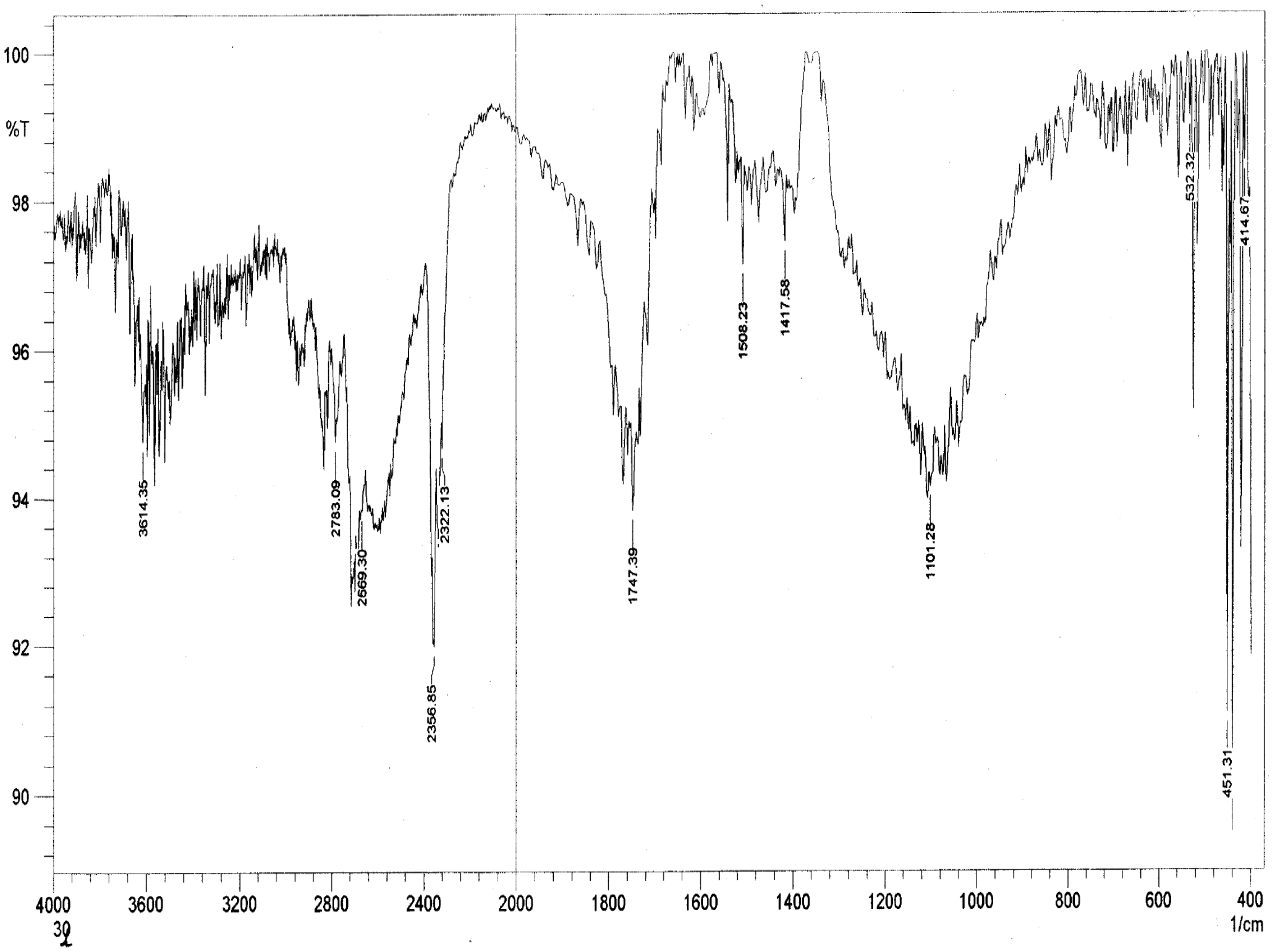


Fig. 1a. FT-IR spectra of native sawdust.

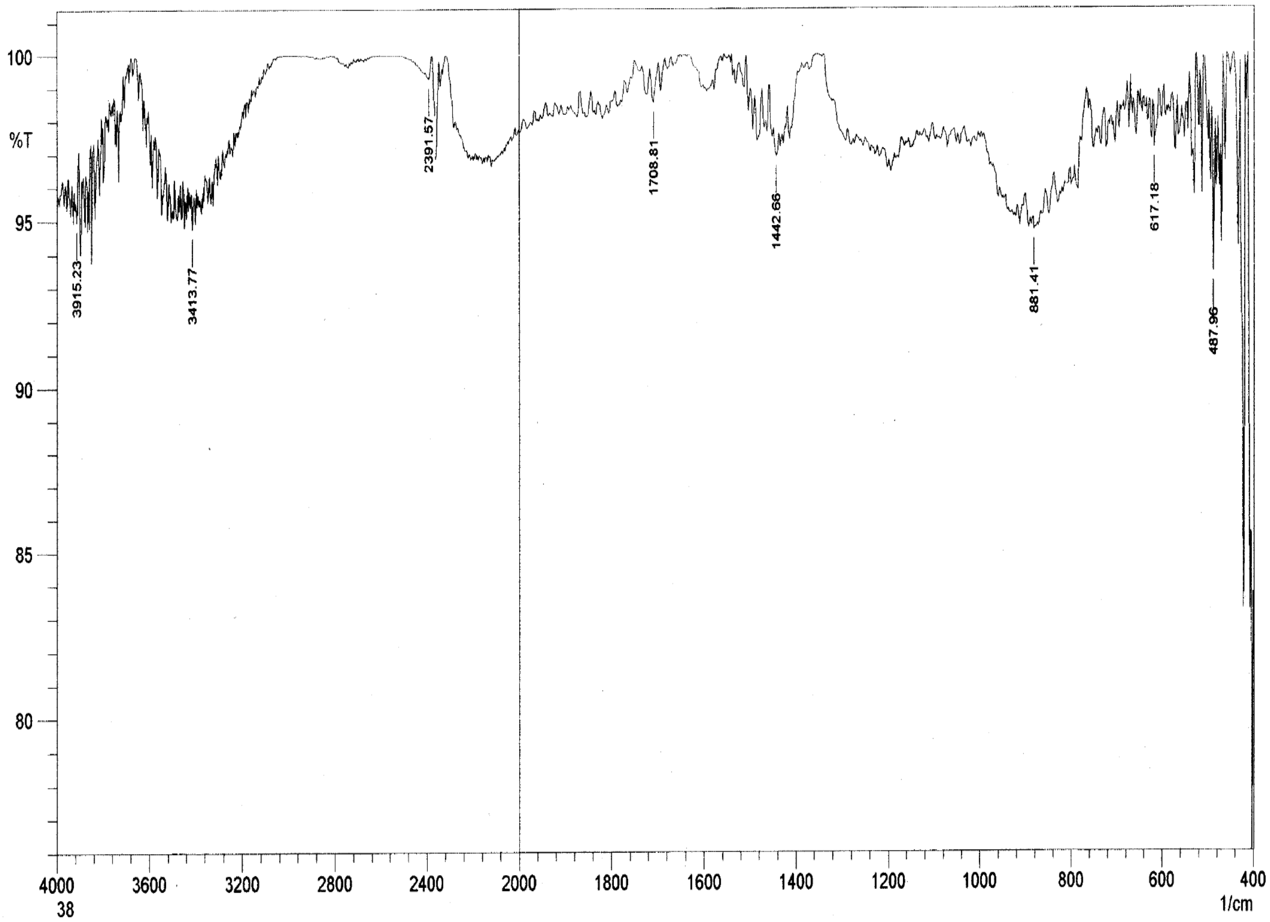
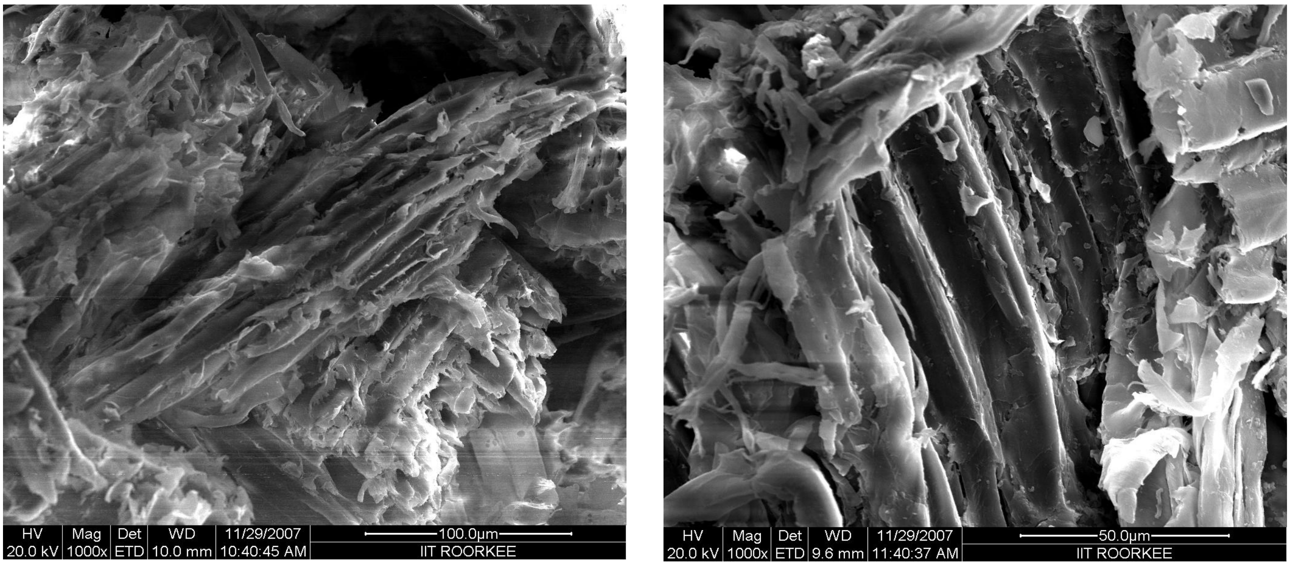


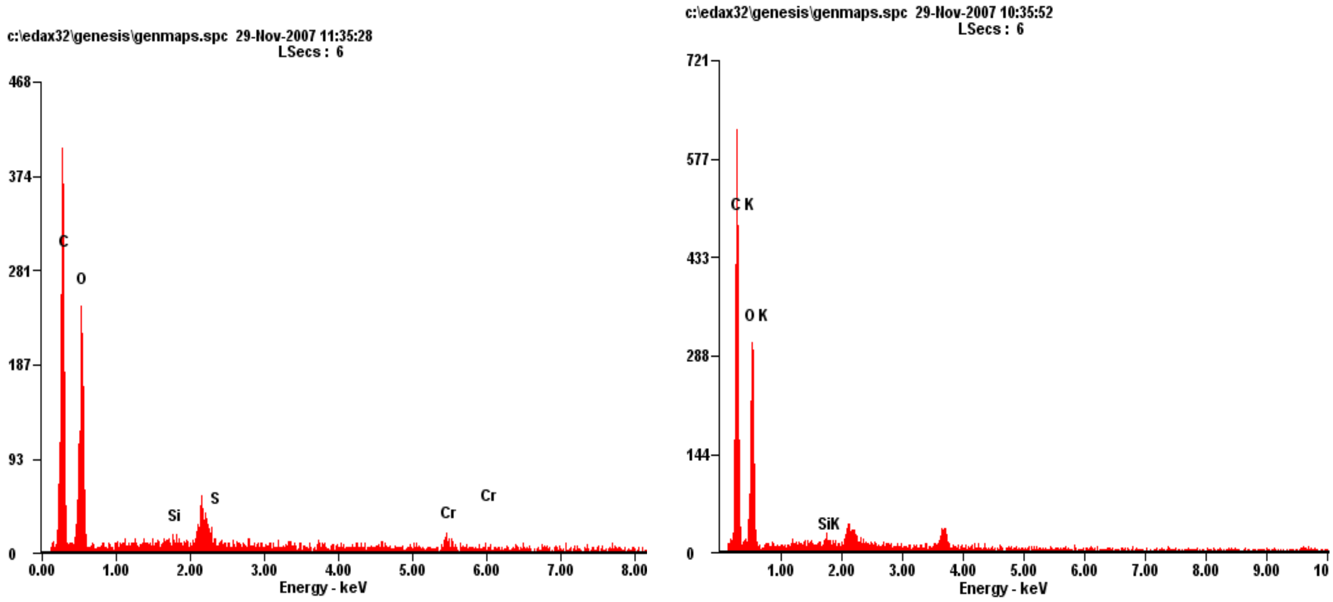
Fig. 1b. FT-IR spectra of Cr(VI)-loaded sawdust.



(a) SEM of native SD

(b)SEM of Cr(VI) loaded SD

Fig. 2a,b. SEM of native and Cr(VI) loaded adsorbent.



(c) EDAX of Cr(VI) loaded SD

(d) EDAX of native SD

Fig. 2c,d. EDAX of native and Cr(VI) loaded adsorbent.

speed = 180 rpm; contact time = 180 min, adsorbent dose = 4 g L^{-1}, temperature = 25°C). There was a sharp decline in % adsorption with increase in pH of the aqueous solution. Chromium adsorption was decreased from 56 to 18.7% as pH was increased from 2 to 7. The maximum adsorption of chromium was 56% at pH 2 (Fig. 3) and hence it was taken as the optimal pH value for further adsorption experiments. Our results are consistent with other workers [14,16–19] that the adsorption of Cr(VI) decrease with the increase of pH (>5.0). The pH dependence of metal adsorption can largely be related to the type and ionic state of the functional groups present on the adsorbent and the Cr(VI) chemistry in solution [19]. In the pH range of 1.0–6.0, chromium ions co-exists in different forms, such as $Cr_2O_7^-$, $HCrO_4^-$, $Cr_3O_{10}^{2-}$, $Cr_4O_{13}^{2-}$ of which $HCrO_4^-$ predominates. As pH of the solution increases then the predominant species are CrO_4^{2-} and $Cr_2O_7^{2-}$. More adsorption at acidic pH indicates that the lower pH results in an increase in H$^+$ ions on the adsorbent surface that result in significantly strong electrostatic attraction between positively charged adsorbent surface and chromate ions. Lesser adsorption of Cr(VI) at pH values greater than 6.0 may be due the dual competition of both the anions (CrO_4^{2-} and OH$^-$) to be adsorbed on the surface of the adsorbent of which OH$^-$ predominates.

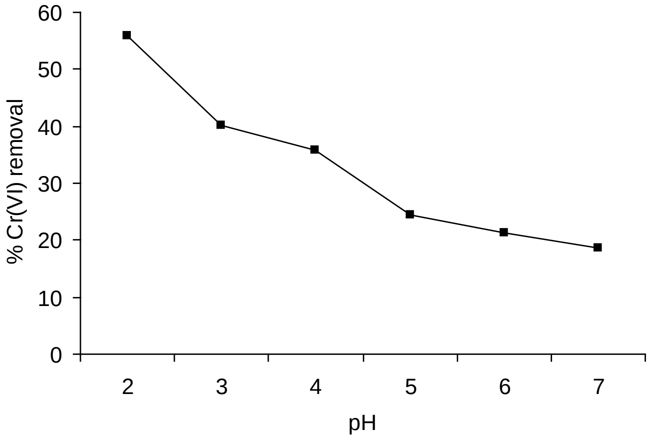


Fig. 3. Effect of pH on Cr(VI) removal by sawdust (Cr(VI) concentration = 50 mg L^{-1}; biosorbent dose = 4g L^{-1}; contact time = 180 min, stirring speed = 180 rpm; temperature = 25°C.

3.4. Effect of initial Cr(VI) concentration and contact time

Effect of contact time and initial concentration on Cr(VI) removal at 25°C and pH 2.0 was studied. The results so obtained are given in Fig. 4. It is evident from the results that % adsorption of metal ion increases rapidly with time and attains equilibrium at about 120 min for all the concentrations studied (10–70 mg L^{-1}). The % adsorption of metal ion is inversely related to the initial metal ion concentrations. Percentage of Cr(VI) removal was decreased as its concentration was increased at fixed adsorbent dose. The removal of Cr(VI) was dependent on the initial concentration. At low concentration, the ratio of available surface to the initial Cr(VI) concentration is larger, so the removal is higher. However, in the case of higher concentrations this ratio is low; hence the percentage removal is also lesser. But the amount of Cr(VI) ions adsorbed per unit mass of adsorbent increased with the

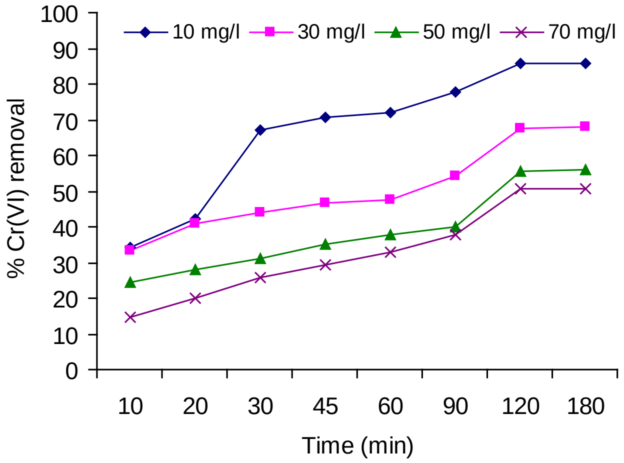


Fig. 4. Effect of initial concentration and contact time on Cr(VI) removal by sawdust (biosorbent dose = 4 g L^{-1}; pH = 2, stirring speed = 180 rpm; temperature = 25°C).

increase of the initial ion concentrations. When the Cr(VI) ion concentration was increased from 10 to 70 mg L^{-1}, the adsorption capacity of sawdust increased from 2.15 to 8.87 mg g^{-1} at equilibrium (Table 2).

3.5. Effect of adsorbent dose and contact time

Cr(VI) removal at different adsorbent doses was studied by varying the adsorbent dose from 4 to 20 g L^{-1} while keeping the concentration of the metal solution constant at 25°C temperature and 2.0 pH. It is evident from Fig. 5 that % adsorption of Cr(VI) ion was increased with time as well as adsorbent dose. This is because of the availability of more and more adsorption sites for complexation of Cr(VI) ions with increase in adsorbent dose [19]. Time required for the equilibrium attainment was 120 min. However, the unit adsorption capacity showed a reverse trend to the % adsorptions. With increasing adsorbent dose from 4 to 20 g L^{-1}, the adsorption capacity of adsorbent decreased from 10.9 to 4.00 mg g^{-1} (Table 2). This is due to overlapping and aggregation of adsorption sites when absorbbent dose increased from 4 to 20 g L^{-1} [13].

3.6. Adsorption isotherms

The Langmuir, Freundlich and Dubinin–Radushkevich (D–R) models have been employed as adsorption isotherm models. These isotherms relate the amount of solute adsorbed at equilibrium per unit weight of adsorbent, x/m (mg g^{-1}), to the adsorbate concentration at equilibrium, C_e (mg L^{-1}).

The Langmuir model represents one of the first theoretical treatments of non-linear sorption and suggests that the uptake occurs on a homogenous surface by monolayer sorption without interaction between the adsorbed molecules. The linear form of the Langmuir adsorption isotherm is represented as:

$$C_e / q_e = [1/Q_0 b + 1/Q_0 \times C_e] \quad (3)$$

where C_e is the equilibrium concentration of adsorbate (mg L^{-1}), and q_e is the amount of Cr(VI) adsorbed per gram at equilibrium (mg g^{-1}). Q_0 (mg g^{-1}) and b (L mg^{-1}) are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. The values of Q_0 and b were calculated from the slope and intercept of the Langmuir plot of C_e vs. C_e/q_e. The essential characteristics of Langmuir isotherm can be expressed in terms of dimensionless constant separation factor for equilibrium parameter, R_L [20] which is defined as given below:

Table 2
Adsorption capacity of sawdust at different initial Cr(VI) concentrations and different adsorbent doses

Parameter	Adsorption capacity (q_e, mg g^{-1})
Initial Cr(VI) concentration (mg L^{-1})	
10	2.15
30	5.08
50	7.00
70	8.87
Adsorbent dose (g L^{-1})	
4	10.90
8	6.80
12	4.98
16	4.76
20	4.00

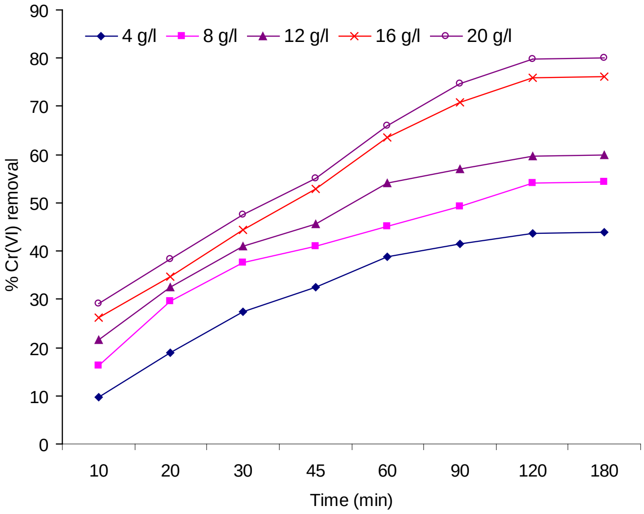


Fig. 5. Effect of biosorbent dose and contact time on Cr(VI) removal by sawdust (Cr(VI) concentration = 100 mg L^{-1}; pH = 2; stirring speed = 180 rpm; temperature = 25°C.

$$R_L = 1/\left(1+bC_0\right) \tag{4}$$

where b is the Langmuir constant (L mg^{-1}) and C_0 (mg L^{-1}) is the initial concentration of Cr(VI).The R_L parameter is considered as a reliable indicator of the adsorption. There are four probabilities for the value of R_L: (i) for favorable adsorption, $0 < R_L < 1$, (ii) for unfavorable adsorption, $R_L > 1$, (iii) for linear adsorption, $R_L = 1$, (iv) for irreversible adsorption, $R_L = 0$ .The values of R_L for the studied system at different initial concentrations were found to be in between 0 and 1 which indicates favorable adsorption of Cr(VI) onto the adsorbent (Table 4).

The Freundlich model can be applied for non-ideal sorption onto heterogeneous surfaces involving multilayer sorption. The linearized Freundlich isotherm was applied for the adsorption of Cr (VI) and is expressed as:

$$\log_{10} q_e = \log_{10}\left(K_f\right) + (1/n)\log_{10}\left(C_e\right) \tag{5}$$

where q_e is the amount of Cr(VI) adsorbed at equilibrium (mg g^{-1}), and C_e is the equilibrium concentration of chromium in solution (mg L^{-1}). K_f and n are the constants incorporating all factors affecting the adsorption process (adsorption capacity and intensity). Values of K_f and n were calculated from the intercept and slope of the plot and are given in Table 3. K_f and n both affect the adsorption process. The larger the K_f and n values, the higher the adsorption capacity. The magnitude of the exponent n gives an indication of the favorability of the adsorption. It is generally stated that values of n in the range 2–10 represent good, 1–2 moderately difficult and less than one poor adsorption characteristics [21]. Results of Langmuir and Freundlich isotherm are summarized in Table 3. According to the coefficient of correlation both models fitted well. The adsorption capacity of the adsorbent indicates potential for the removal of the Cr(VI) from dilute wastewaters. Value of slope found to be lesser than unity implied that significant adsorption took place at low metal ion concentration [22].

The Dubinin–Radushkevich (D–R) model was also applied to the equilibrium data to determine if sorption had occurred by physical or chemical processes [23,24]. The D–R adsorption isotherm is represented as:

$$\log_{10} q_e = \log_{10} q_D - 2B_D R^2 T^2 \log_{10}\left(1+1/C_e\right) \tag{6}$$

where q_D is theoretical saturation capacity (mg g^{-1}) and B_D is a constant related to adsorption energy (mol^{2}KJ^{-2}), R is the gas constant (kJ mol^{-1}K^{-1}) and T is the temperature (K). The slope of the plot $\log_{10} q_e$ vs. $\log_{10} (1 + 1/C_e)$ gives the q_D and B_D values. The constant B_D gives an idea about the mean free energy E_D (kJ mol^{-1}) 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 B_D using following equation [20]:

$$E_D = 1/\sqrt{2B_D} \tag{7}$$

This sorption energy is independent of the temperature but varies depending on the nature of the adsorbent and adsorbate [23]. The magnitude of E_D provides information on the nature of the sorption process, i.e. whether it is chemical or physical, with values in the range E_D = 1–8 kJ mol^{-1} corresponding to physical sorption and in the range 8–16 kJ mol^{-1} to chemisorption [23,24]. The calculated E_D value was found to be 1.54 kJ mol^{-1} (Table 3). E_D value less than 8 KJ mol^{-1} as indicated by our results shows that the adsorption process of Cr(VI) on sawdust follows physical adsorption.

Table 3
Langmuir, Freundlich and Dubinin–Radushkevich model's regression constants for sawdust

Langmuir isotherm	
Q_0 (mg g^{-1})	10.34
B (L mg^{-1})	0.13
R^2	0.966
Freundlich isotherm	
K_f (mg g^{-1})	1.84
n (L mg^{-1})	2.26
R^2	0.999
D–R isotherm	
q_D (mg g^{-1})	7.79
B_D (mol^2 KJ^{-2})	0.21
E_D (KJmol^{-1})	1.54
R^2	0.937

Table 4
Separation factor (R_L) of sawdust at different initial concentrations of Cr(VI)

Initial Cr(VI) concentration (mg L^{-1})	Separation factor (R_L)
10	0.43
30	0.20
50	0.13
70	0.10

3.7. *Adsorption kinetic study*

In the present study, pseudo-first-order and pseudo-second-order kinetic models have been tested at different concentrations. The first-order-model can be expressed as follows:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303}t \tag{8}$$

where q_e (mg g^{-1}) is the mass of Cr(VI) adsorbed at equilibrium, q_t (mg g^{-1}) the mass of Cr(VI) at any time and k_1 (min^{-1}) is the equilibrium rate constant of pseudo-first-order adsorption. The values of k_1 and q_e are determined from the slope and intercept of the plot of log ($q_e - q_t$) vs. t, respectively and are given in Table 5.

The pseudo-second-order model, which leads to the following equation:

$$\frac{t}{q_t}=\frac{1}{k_2 q_e^{2}}+\frac{1}{q_e}t \tag{9}$$

where k_2 is the pseudo-second-order rate constant (g mg^{-1}min^{-1}) The value of q_e is determined from the slope of the plot of t/q_t vs. t. The calculated q_e value from the pseudo-second-order model is in good agreement with experimental q_e value. This suggests that the sorption system followed the pseudo second-order model.

3.8. Desorption studies

Desorption studies are helpful to explore the possibility of recycling the adsorbent and recovery of the metal resource. Desorption experiments were done at contact time of 60 min at different concentration (0.0125–0.150 M). KI and HCl solutions were tested to remove metal from the adsorbent. Desorption results for studied adsorbent by KI and HCl solutions are shown in Fig. 6. Desorption was 60.67% by KI solution and 79.63% by HCl solution at 0.150 M concentrations for the studied adsorbent, respectively.

4. Conclusions

In this study removal of Cr(VI) on sawdust has been investigated. The Cr(VI) removal process is significantly affected by various process parameters, namely, pH, adsorbent dose, metal ion concentration and contact time. Maximum removal of Cr(VI) on sawdust was at pH 2.0. Cr(VI) sorption follows Freundlich model than Langmuir model and Dubinin–Raduskevich model indicates physical adsorption. Pseudo second order model has explained the Cr(VI) kinetics more effectively than pseudo first order. Desorption studies indicates good reusability of the adsorbent. Sawdust is easily available in the countryside, so can be used by small scale industries having low concentrations of Cr(VI) in wastewater using batched reactors. The kinetic data obtained from the adsorption studies will be useful for fabrication and design of wastewater treatment plants.

Table 5
Kinetic parameters for the removal of Cr(VI) by sawdust

Parameter	Kinetic parameters
Pseudo first order	
q_e, exp (mg g^{-1})	10.95
k_1 (min^{-1})	0.02
q_e, cal (mg g^{-1})	5.78
R^2	0.48
Pseudo second order	
q_e, exp (mg g^{-1})	10.95
k_2 (g mg^{-1} min^{-1})	0.0023
q_e, cal (mg g^{-1})	13.48
R^2	0.98

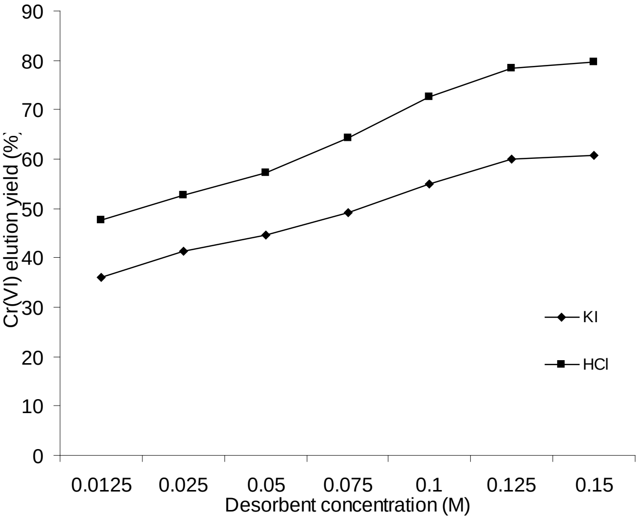


Fig. 6. Desorption of the Cr(VI) from sawdust by KI and HCl.

References

[1] G. Cimino and C. Caristi, Acute toxicity of heavy metals to aerobic digestion of waste cheese whey. Biological Wastes, 33 (1990) 201–210.

[2] P. Madoni, D. Davoli, G. Gorbi and L. Vescovi, Toxic effect of heavy metals on the activated sludge protozoan community. Water Res., 30 (1996) 135–142.

[3] J. Goel, K. Kadirvelu, C. Rajagopal and V.K. Garg, Removal of lead (II) by adsorption using treated granular activated carbon: batch and column studies. J. Hazard. Mater., B125 (2005) 211–220.

[4] C. Raji and T.S. Anirudhan, Batch Cr(VI) removal by polyacrylamidegrafted sawdust: kinetics and thermodynamics. Water Res., 32 (1998) 3772–3780.

[5] F. Gode and E. Pehlivan, Removal of chromium(III) from aqueous solutions using Lewatit S 100: The effect of pH, time, metal concentration and temperature. J. Hazard. Mater., 136 (2006) 330–337.

[6] B.M. Braukman, Industrial solutions amenable to biosorption, in: B. Volesky, ed., Biosorption of Heavy Metals, CRC Press, USA, 1990, pp. 51–64.

[7] A. Ozer, H.S. Altundogan, M. Erdem and F. Tumen, A study on the Cr (VI) removal from aqueous solutions by steel wool. Environ. Pollut., 97(1–2) (1997) 107–112.

[8] M. Lotfi and N. Adhoum, Modified activated carbon for the removal of copper, zinc, chromium and cyanide from wastewater. Separ. Purif. Technol., 26 (2002) 137–146.

[9] C. Namasivayam and R.T. Yamuna, Adsorption of chromium (VI)

by a low-cost adsorbent: biogas residual slurry. Chemosphere, 30 (1995) 561–578.

[10] S. Rengaraj, C.K. Joo, Y. Kim and J. Yi, Kinetics of removal of chromium from water and electronic process wastewater by ion exchange resins: 1200H, 1500H and IRN97N. J. Hazard. Mater., B102 (2003) 257–275.

[11] A.P. Padilla and E.L. Tavani, Treatment of an industrial effluent by reverse osmosis. Desalination, 129 (1999) 219–226.

[12] R.S. Bai and T.E. Abraham,. Studies on chromium (VI) adsorptione desorption using immobilized fungal biomass. Bioresour. Technol., 87 (2003) 17–26.

[13] V.K. Garg, R. Gupta, R.K. Gupta and R. Kumar, Adsorption of chromium from aqueous solution on treated sawdust, Bioresour. Technol., 92 (2004) 79–81.

[14] L. Zhang, L. Zhao, Y. Yu and C. Chen, Removal of lead from aqueous solution by non-living *Rhizopus nigricans.* Water Res., 32 (1998) 1437–1444.

[15] A. Kapoor and T. Viraraghavan, Removal of heavy metals using the fungus *Aspergillus niger.* Bioresour. Technol., 70 (1999) 95–104.

[16] Z. Aksu, Equilibrium and kinetic modelling of cadmium (II) biosorption by *C. vulgaris* in a batch system: effect of temperature. Separ. Purif. Technol., 21 (2001) 285–294.

[17] C.P. Huang and M.H. Wu, The removal of chromium (VI) from dilute aqueous solution by activated carbon. Water Res., 11 (1977) 673–679.

[18] T. Karthikeyan, S. Rajgopal and L.R. Miranda, Chromium (VI) adsorption from aqueous solution by Hevea Brasilinesis sawdust activated carbon. J. Hazard. Mater., B124 (2005) 192–199.

[19] K. Mohanty, M. Jha, B.C. Meikap and M.N. Biswas, Biosorption of Cr(VI) from aqueous solutions by *Eichhornia crassipes.* Chem. Eng. J., 117 (2006) 71–77.

[20] K.R. Hall, L.C. Eagleton, A. Acrivos and T. Vermeulen, Pore and solid diffusion kinetics in fixed bed adsorption under constant pattern conditions. Indian Eng. Chem. Fundam., 5 (1966) 212–218.

[21] R.E. Treybal, Mass-Transfer Operations, 3rd ed., McGraw Hill, 1981.

[22] U.K. Garg, M.P. Kaur, V.K. Garg and D. Sud,. Removal of nickel (II) from aqueous solution by adsorption on agricultural waste biomass using a response surface methodological approach. Bioresour. Technol., 99(5) (2008) 1325–1331.

[23] R. Donat, A. Akdogan, E. Erdem and H. Cetisli, Thermodynamics of Pb^{2+} and Ni^{2+} adsorption onto natural bentonite from aqueous solution, J. Colloid Interf. Sci., 286 (2005) 43–52.

[24] M.M. Dubinin, E.D. Zaverina and L.V. Radushkevich, Sorption and structure of active carbons. I. Adsorption of organic vapors, Zhurnal Fizicheskoi Khimii, 21 (1947) 1351–1362.