

Hexavalent chromium removal from aqueous solution by adsorption on treated sawdust

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Abstract

The studies on adsorption of hexavalent chromium were conducted by varying various parameters such as contact time, pH, amount of adsorbent, concentration of adsorbate and temperature. The kinetics of adsorption of Cr(VI) ion followed pseudo second order. Langmuir adsorption isotherm was employed in order to evaluate the optimum adsorption capacity of the adsorbent. The adsorption capacity was found to be pH dependant. Sawdust was found to be very effective and reached equilibrium in 3 h (adsorbate concentration 30 mg l⁻¹). The rate constant has been calculated at 303, 308, 313 and 318 K and the activation energy (E_a) was calculated using the Arrhenius equation. Thermodynamic parameters such as standard Gibbs energy (ΔG°) and heat of adsorption (ΔH_r) were calculated. The ΔG° and ΔH_r values for Cr(VI) adsorption on the sawdust showed the process to be exothermic in nature. The percentage of adsorption increased with decrease in pH and showed maximum removal of Cr(VI) in the pH range 4.5–6.5 for an initial concentration of 5 mg l⁻¹.

Keywords: Adsorption; Cr(VI); Treated sawdust; Kinetics; Isotherm and thermodynamics

1. Introduction

Rapid industrialization and increase in population are responsible for the inclusion of heavy metals in the environment. As a consequence, these metals are found well above the tolerance limit many a times in aquatic environment [1]. Chromium is widely used in electroplating, leather tanning, dye, cement and photography industries producing large quantities of effluents containing the toxic metal [2]. The Cr(VI) is of particular concern because of its toxicity [3]. The recommended limit of Cr(VI) in potable water is only 0.05 mg l⁻¹ [4]. But the industrial and mining effluents contain much higher concentrations compared to the permissible limit. Thus, treatment of the effluent to reduce/remove the pollutant before discharging into the environment becomes inevitable.

Different methods such as reduction and precipitation [5], ion exchange [6], electrolysis, reverse osmosis, solvent extraction [7], adsorption [8], and electrochemical precipitation [9] have been suggested for the removal of Cr(VI). Among all these,

adsorption is the most promising technique and a feasible alternative [10]. A variety of materials have been tried as adsorbents for Cr(VI) and a number of studies have been reported using adsorbents like granular activated carbon [11], Soya cake [12], rubber tyres and sawdust [13], activated sludge [14], lingo-cellular substrate [15], fly ash [16], rice husk based activated carbon [17], etc.

In the present work, the Cr(VI) adsorption capacity of sawdust derived from *Shorea robusta* (*Sal*) was studied. The well-known thermodynamic functions and isotherm studies have been reported to elucidate the equilibrium adsorption behavior at different temperatures. In addition to the effect of temperature, the effect of pH, adsorbent dose, time and concentration of adsorbate on percentage of adsorption have also been investigated.

2. Experimental

2.1. Preparation and characterization of adsorbent

The sawdust *S. robusta* (*Sal*) used in this experiment was collected from a local sawmill and dried in sunlight until almost all the moisture evaporated. It was ground to a fine powder and sieved to 125–250 μm size. Sawdust contained water-soluble

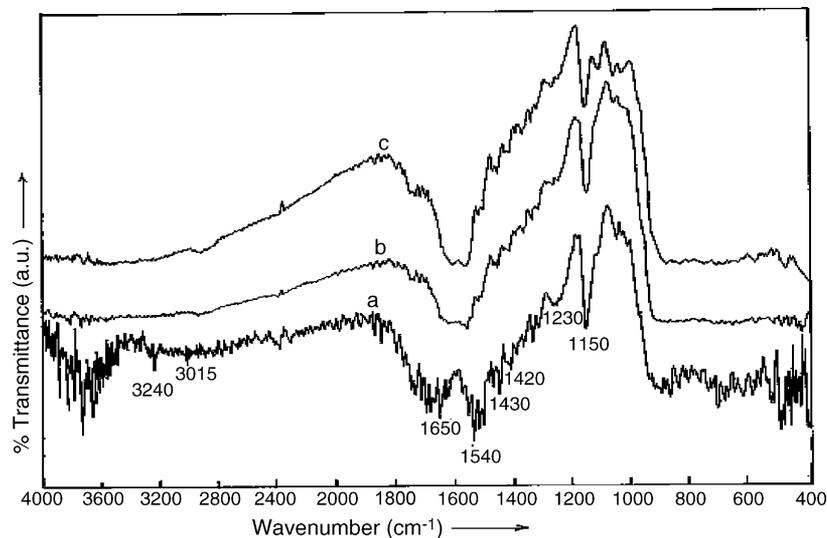


Fig. 1. FTIR spectra of (a) untreated sawdust, (b) treated sawdust and (c) treated sawdust after adsorption.

compounds like tannin, which gave brown color to the effluents during the treatment. Chemical treatment with formaldehyde led to polymerization of the compounds responsible for colorization. Sawdust (50 g) was washed repeatedly with distilled water and subsequently dried for 24 h at 233 K to washout the coloring materials. To improve upon the physical characteristics further, it was treated with 1% formaldehyde in the ratio of 1:4 (sawdust:formaldehyde, w/v) and 100 ml of 0.2N H_2SO_4 . It was heated with cover-over hotplate at 323 K for 6 h with occasional stirring. The product was cooled and washed several times with distilled water and finally dried at 333 K to eliminate all toxicity due to the presence of formaldehyde.

The sawdust sample (10 mg) was ground with 200 mg of KBr (spectroscopic grade) in a mortar pressed into 10 mm diameter disks under 10 tonnes of pressure and high vacuum for 10 min. FTIR spectra were obtained on a JASCO FTIR-3500 spectrometer. The analysis conditions used were 16 scans at a resolution of 4 cm^{-1} measured between 400 and 4000 cm^{-1} . The FTIR spectra of sawdust, treated sawdust and the sawdust after adsorption are shown in Fig. 1. The FTIR spectra of sawdust showed peaks at 3240, 3015, 1650, 1540, 1450, 1420 1250 and 1160 cm^{-1} which may be assigned to OH group, aliphatic C–H group, unsaturated groups like alkene, amide, CH deformation, OH deformation, aromaticity and OH stretch, respectively. The intensity of the peaks were either minimized or shifted slightly in case of treated and adsorbed sawdust, respectively. These results are similar to the ones reported earlier [18]. Due to the limitation of the instrument, we could not undertake the spectral analysis in the far IR, which might have showed the evidences of Cr–N, Cr–S or Cr–O vibrations.

2.2. Adsorption

Adsorption experiments were conducted by varying contact time, pH, adsorbent dose and adsorbate concentration. The experiments were carried out in 100 ml conical flasks and the total volume of the reaction mixture was kept at 50 ml. The pH

of solution was maintained at a desired value by adding 0.1 M NaOH or HCl. The conical flasks were shaken for the required time period in a Yorko thermostatic water bath. The mixture was filtered through Whatman No. 42 filter paper and the final volume made to 50 ml. The equilibrium concentration of Cr(VI) in the solution was determined by reacting with 1,5-diphenyl carbazide and the absorption was measured in a Chemito-2500 Recording UV-Visible Spectrophotometer at 540 nm. In these experiments, all chemicals used were of AR/GR grade.

3. Result and discussion

3.1. Effect of adsorbent dose

Four different adsorbents such as alumina, goethite, alum sludge and sawdust were taken to compare the efficiency of the treated sawdust with respect to the others adsorbents. It is evident from Fig. 2 that the efficiency of sawdust to remove

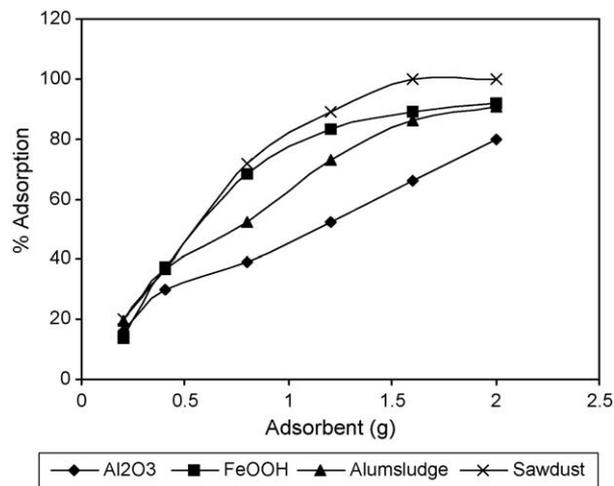


Fig. 2. Adsorption of Cr(VI) by different adsorbents [conditions: time 1 h, adsorbate 2.72 mg g^{-1} , temperature 303 K, pH 7].

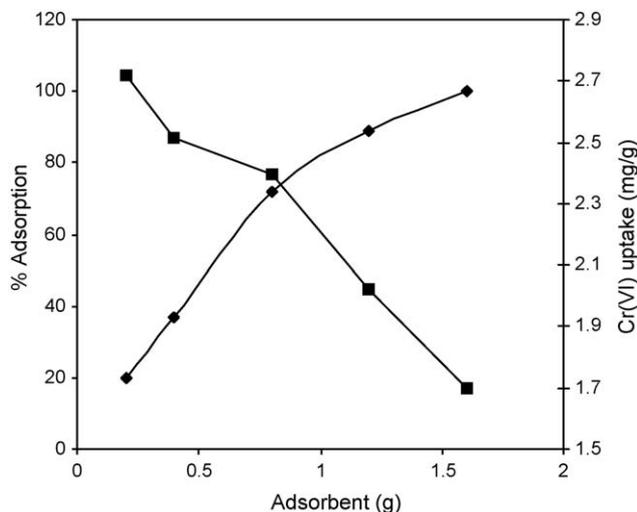


Fig. 3. Effect of adsorbent dose on percentage adsorption and uptake [conditions: time 1 h, adsorbate 2.72 mg g^{-1} , temperature 303 K, pH 7].

Cr(VI) was the highest among them. The percentage adsorption increased with increase in adsorbent dose. This is evident from Fig. 3, where percentage adsorption was plotted against adsorbent dose. The percentage adsorption increased from 20 at lower adsorbent dose (0.2 g l^{-1}) to 100 at higher adsorbent dose (1.6 g l^{-1}). However, the Cr(VI) uptake capacity of the sawdust was found to have reduced from 2.72 mg g^{-1} at low adsorbent dose (0.2 g l^{-1}) to 1.7 mg g^{-1} at high adsorbent dose (1.6 g l^{-1}) in Fig. 3. Similar trend has also been reported by other investigators in Cr(VI) sorption [19]. The decrease in Cr(VI) uptake at higher adsorbent dose may be due to competition of the Cr(VI) ion for the sites available.

3.2. Effect of initial adsorbate concentration

Analysis of percentage adsorption and loading capacity versus initial concentration (Fig. 4) were studied at varying contact

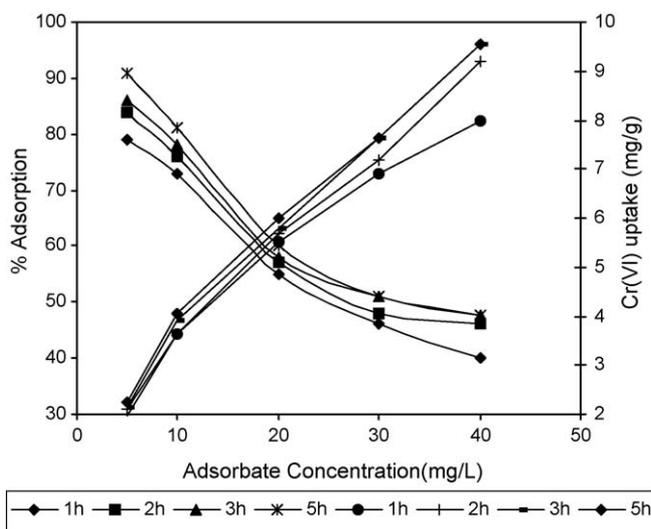


Fig. 4. Effect of adsorbate concentration on percentage adsorption and Cr(VI) uptake at different time [conditions: adsorbent 0.1 g , pH 3.5, temperature 303 K].

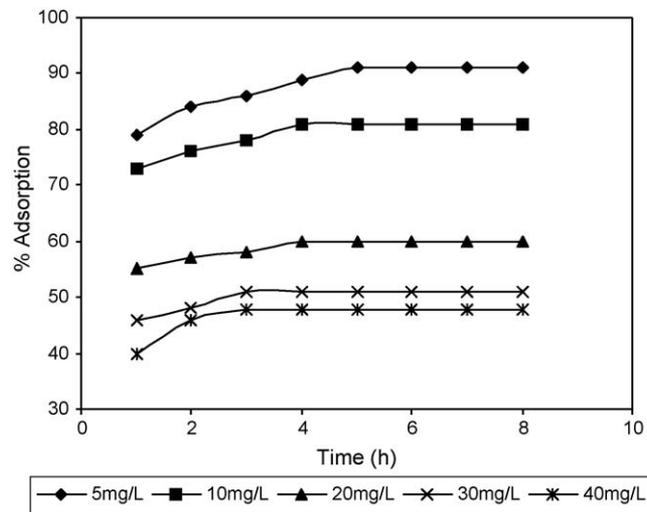


Fig. 5. Effect of contact time on percentage adsorption at different adsorbate concentration [conditions: adsorbent 0.1 g , pH 3.5, temperature 303 K].

time and it was found that the percentage adsorption decreased with increase in initial concentration of the adsorbate. But the uptake capacity increased with increase in initial concentration, which may be due to the availability of more number of Cr(VI) ions in solution for sorption. Moreover, higher initial adsorbate concentration provided higher driving force to overcome all mass transfer resistances of the metal ions from the aqueous to the solid phase resulting in higher probability of collision between Cr(VI) ions and the active sites. This also resulted in higher uptake of Cr(VI) for the given amount of treated sawdust.

3.3. Effect of contact time

A plot of percentage adsorption versus adsorption time is shown in Fig. 5. It is evident from the figure that the equilibrium time is dependant on the adsorbate concentration. The equilibrium time was varied from 2 h at higher adsorbate concentration (40 mg l^{-1}) to 5 h at low adsorbate concentration (5 mg l^{-1}). All the curves obtained were smooth indicating formation of monolayer on the surface of the adsorbent. In the initial stage, the slope of the plot was 1 and it decreased with time. It revealed that the rate of uptake was rapid in the early stages but gradually decreased and became constant when equilibrium was reached.

3.4. Effect of temperature

Temperature has an importance effect on the process of adsorption. The percentage of Cr(VI) adsorption was studied as a function of temperature in the range of 303–318 K. The results obtained are presented in Fig. 6. The decrease in percentage of adsorption with rise in temperature may be due to the desorption caused by an increase in the available thermal energy. Higher temperature induces higher mobility of the adsorbate causing desorption.

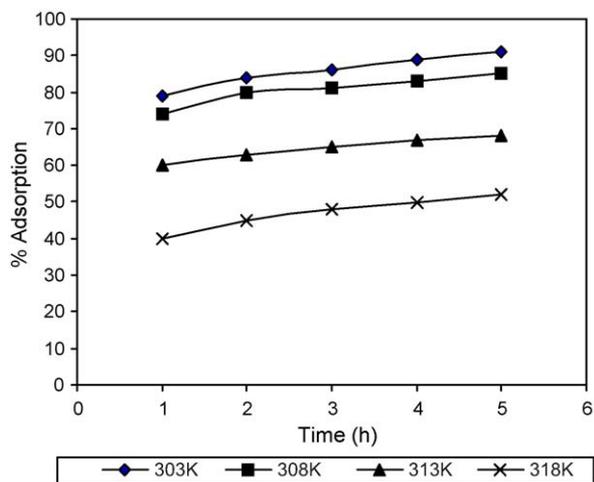


Fig. 6. Effect of temperature on percentage adsorption at different time [conditions: adsorbent 0.1 g, adsorbate 5 mg l^{-1} , pH 3.5].

3.5. Effect of pH

The adsorption experiment was carried out in the concentration range of 2.72 mg l^{-1} (mine water) to 10 mg l^{-1} (synthetic solution) as a function of equilibrium pH and is shown in Fig. 7. It is evident from this figure that the percentage adsorption is higher at lower pH, reaching maximum at the pH range 4.5–6. But it decreased with increase in pH and became constant at $\text{pH} > 9.0$. The effect of pH on the adsorption capacity of treated sawdust may be attributed to the combined effect of the nature of the surface, amount of adsorbed Cr(VI) species. To explain the observed behavior of Cr(VI) adsorption with varying pH, it is necessary to examine various mechanisms such as electrostatic attraction/repulsion, chemical interaction and ion exchange, which are responsible for adsorption on adsorbent surfaces.

From the stability diagram [19], it was observed that the most prevalent form of Cr(VI) in aqueous solution was acid chromate

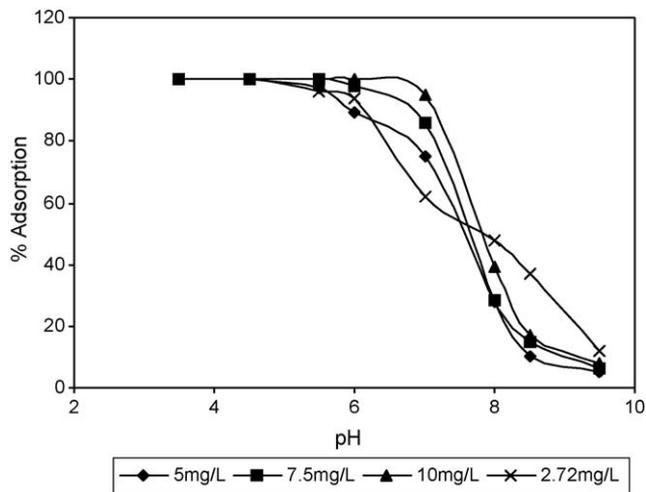


Fig. 7. Effect of pH on percentage adsorption at different adsorbate concentration [conditions: adsorbent 0.6 g, time 1 h, temperature 303 K].

(HCrO_4^-), chromate (CrO_4^{2-}), dichromate ($\text{Cr}_2\text{O}_7^{2-}$) and other Cr oxyanions. From the stability diagram of Cr(VI)– H_2O system, it was evident that at low pH, acid chromate ions (HCrO_4^-) are the dominant species. As the pH increased, there was little increase in the percentage of adsorption and it was maximum at pH 4.5. When the pH is further increased, a sharp decrease in percentage of adsorption was observed. This might be due to the weakening of electrostatic force of attraction between the oppositely charged adsorbate and adsorbent and ultimately lead to the reduction in sorption capacity. When the pH was increased beyond 6.0, a gradual decrease in the percentage adsorption was observed. This might be due to the competition between OH^- and chromate ions (CrO_4^{2-}), where the former being the dominant species wins the race. The net positive surface potential of the sorbent decreased with increasing pH resulting in weakening of electrostatic force between adsorbate and adsorbent which ultimately led to the lowering of sorption capacity. The pH at point zero charge (pzc) was found to be 9.0. This is in agreement with our experimental observations showing a very low adsorption at $\text{pH} > 9$.

4. Adsorption kinetics modeling

The adsorption kinetic models are important in the process of removal of toxic heavy metals from the aquatic environment. In this study of a batch reaction, different reversible models were tested.

4.1. First order reversible reaction model

The sorption of Cr(VI) on treated sawdust may be considered as a first order reversible reaction [20], which can be expressed as



The rate equation for the reaction is expressed as

$$\begin{aligned} \frac{dC_B}{dt} &= -\frac{dC_A}{dt} \\ &= k_1 C_A - k_2 C_B \\ &= k_1 (C_{A0} - C_{A0} X_A) - k_2 (C_{B0} - C_{A0}) \end{aligned} \quad (2)$$

where C_A (mg l^{-1}) and C_B (mg g^{-1}) are the concentrations of Cr(VI) in solution and sorbent, respectively, at a given time 't'; C_{A0} and C_{B0} are the initial concentrations of adsorbate and adsorbent, respectively; k_1 and k_2 are the first order rate constants. At equilibrium

$$K_c = \frac{C_{Be}}{C_{Ae}} = \frac{k_1}{k_2} \quad (3)$$

where K_c is the equilibrium constant and C_{Ae} and C_{Be} are the equilibrium concentrations of Cr(VI) in adsorbate and adsorbent, respectively. Applying the equilibrium conditions, Eq. (2) becomes

$$\ln(1 - U_t) = -(k_1 + k_2)t \quad (4)$$

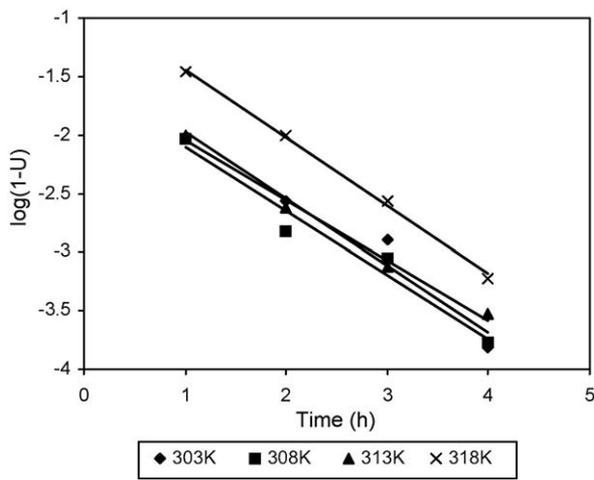


Fig. 8. First order reversible reaction kinetics plot for adsorption of Cr(VI) at different temperatures [conditions: adsorbent 0.1 g, adsorbate 5 mg l⁻¹, pH 3.5].

where U_t is the fractional attainment of equilibrium and is given by

$$U_t = \frac{C_{A0} - C_A}{C_{A0} - C_{Ae}} \quad (5)$$

The plot for the first order reversible kinetics as shown in Eq. (4) was drawn for sawdust at different temperatures (Fig. 8) where linearity relationship was observed. The correlation coefficients R^2 , K_c , k_1 and k_2 were calculated using Eqs. (3) and (4) for different plot and are shown in the Table 1.

4.2. Pseudo first order model

The sorption kinetics may also be described by the pseudo first order reaction model [21], which is expressed as

$$\frac{dq_e}{dt} = k(q_e - q) \quad (6)$$

where ' q_e ' is the amount of solute adsorbed at equilibrium per unit mass of adsorbent (mg g⁻¹), ' q ' is the amount of solute adsorbed at any given time ' t ' and ' k ' is the rate constant. By using the boundary conditions and simplifying, the Eq. (6) becomes

$$\log(q_e - q) = \log q_e - \frac{k}{2.303}t \quad (7)$$

The plot of $\log(q_e - q)$ versus ' t ' as shown in Eq. (7) was plotted at different temperatures as shown in Fig. 9. The correlation coefficients and rate constants were calculated and are given in Table 2. The correlation coefficients were in good agreement with the pseudo first order kinetics.

Table 1

Temperature (K)	k_1 (min ⁻¹)	k_2 (min ⁻¹)	K_c	R^2
303	5.06	0.4769	0.0943	0.9609
308	2.833	0.4324	0.1527	0.9911
313	1.063	0.4208	0.2266	0.9978
318	0.542	0.2047	0.3776	0.9978

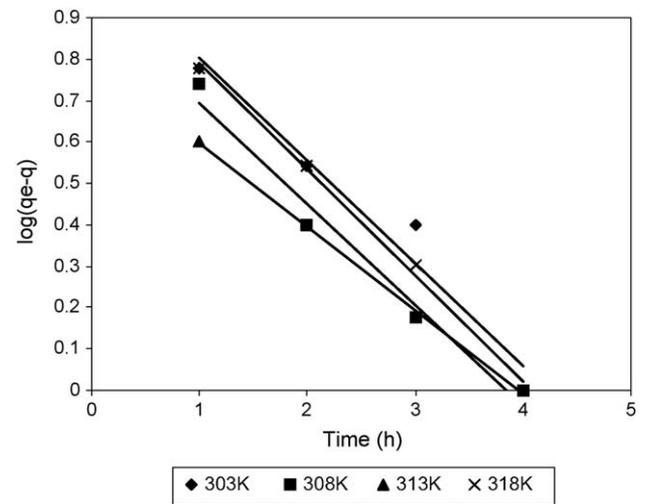


Fig. 9. Pseudo first order reaction kinetics plot for adsorption of Cr(VI) at different temperatures [conditions: adsorbent 0.1 g, adsorbate 5 mg l⁻¹, pH 3.5].

4.3. Pseudo second order reaction

A pseudo second order reaction model [21] may also be applicable to kinetics of sorption and the equation for this reaction is

$$\frac{dq}{dt} = k(q_e - q)^2 \quad (8)$$

This on integration for boundary conditions when $t=0$ to >0 and $q=0$ to >0 and further simplifications, Eq. (8) becomes

$$\frac{t}{q} = \frac{1}{kq_e^2} + \frac{1}{q_e}t = \frac{1}{h} + \frac{1}{q_e}t \quad (9)$$

where $h = kq_e^2$ and is known as initial sorption rate. The kinetics plots of t/q versus t as per Eq. (9) were made at different temperatures (Fig. 10) and the values of correlation coefficients, ' h ' and ' k ', were calculated from the graph as shown in the Table 3.

From the above discussion, it can be concluded that the process of Cr(VI) adsorption in treated sawdust is best fitted to pseudo second order kinetics since the R^2 values matched very well.

5. Adsorption isotherm and thermodynamic parameters

5.1. Langmuir adsorption isotherm

Adsorption studies were carried out with a fixed initial adsorbent dose (0.1 g) and varying adsorbate concentration, and applicability of the data to the Langmuir adsorption isotherm was tested. It was found that the data obtained fitted well into the

Table 2

Temperature (K)	k (min ⁻¹)	R^2
303	0.5711	0.9609
308	0.5622	0.9769
313	0.4668	0.9982
318	0.5935	0.9963

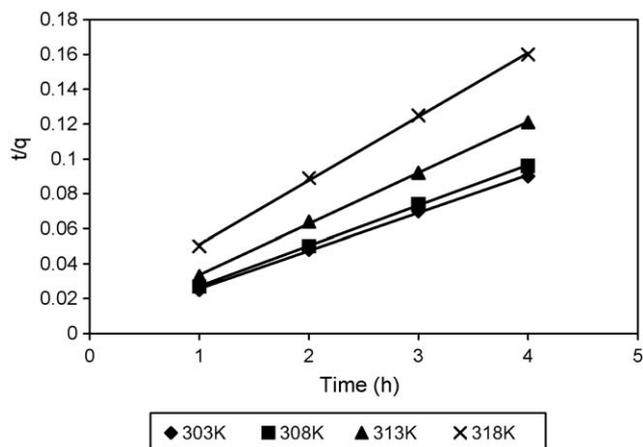


Fig. 10. Pseudo second order reaction kinetics plot for adsorption of Cr(VI) at different temperatures [conditions: adsorbent 0.1 g, adsorbate 5 mg l⁻¹, pH 3.5].

Table 3

Temperature (K)	k (g/mg min)	H (mg/g min)	R^2
303	0.1177	250	0.9994
308	0.1334	250	0.9997
330	0.1895	222.22	0.9996
318	0.0924	68.97	0.9994

linearised Langmuir adsorption isotherm, which is given by

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (10)$$

where C_e is the equilibrium concentration and q_e is the amount adsorbed per gram of adsorbent at equilibrium; Q_0 and b are the Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. The values of Q_0 and b were calculated from the slope and intercept of the graph (Fig. 11) and were found to be 3.6 and 2.36, respectively.

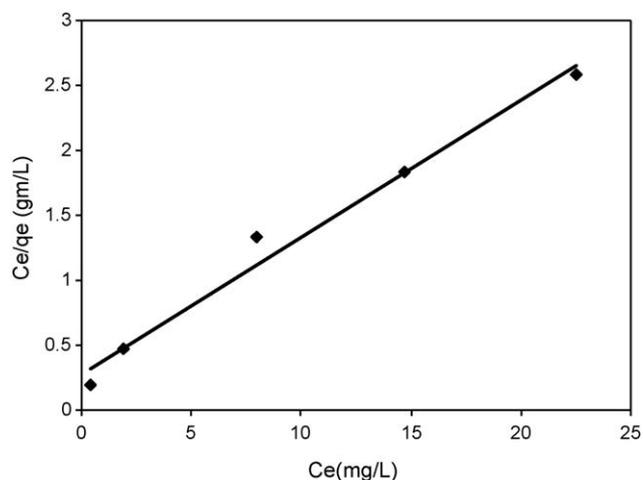


Fig. 11. Langmuir plot for adsorption of Cr(VI).

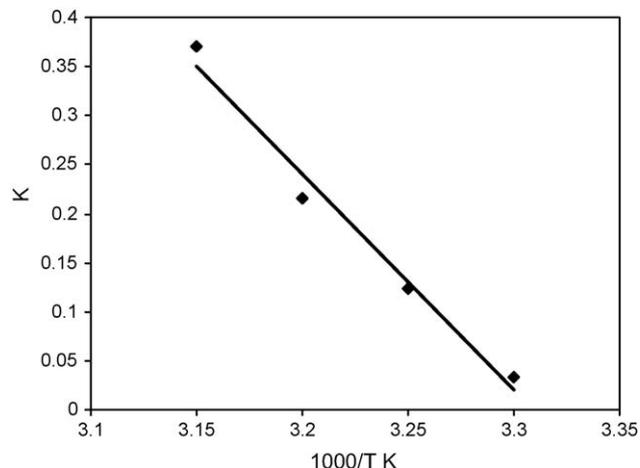


Fig. 12. Arrhenius plot for determination of activation energy.

5.2. Thermodynamic parameters

The activation energy could be calculated by using the Arrhenius equation as

$$\ln k = \ln A - \frac{E_a}{RT} \quad (11)$$

where k is the rate constant at temperature T (K), a pre-exponential factor, R the universal gas constant and E_a (J mol⁻¹) is the activation energy for the process. The $\ln k$ values were plotted against $1000/T$ (K) (Fig. 12) and the activation energy was calculated to be 18.357 kJ mol⁻¹. This low value of activation energy suggested that the adsorption process was governed by the process of diffusion.

The standard Gibbs free energy was calculated by using the following equation:

$$\ln \frac{1}{b} = \frac{\Delta G^\circ}{RT} \quad (12)$$

where b is the Langmuir constant related to the energy of adsorption. The calculated ΔG° value is -746 J g mol⁻¹.

The isosteric heat of adsorption (ΔH_r) is also calculated using the equation:

$$\Delta H_r = \frac{R \ln(C_2/C_1)}{(1/T_2) - (1/T_1)} \quad (13)$$

where C_1 and C_2 are the equilibrium concentrations of adsorbate in the solution at temperatures T_1 and T_2 , respectively and ' R ' is the gas constant. The value of ΔH_r calculated for the temperature range 303–318 K was found to be -2.068 kJ mol⁻¹. The negative value of heat of adsorption (ΔH_r) indicates that the process is exothermic in nature.

6. Mass transfer model

The intra-particle diffusion varies with square root of time [22] as shown below:

$$q_t = k_{id} t^{0.5} \quad (14)$$

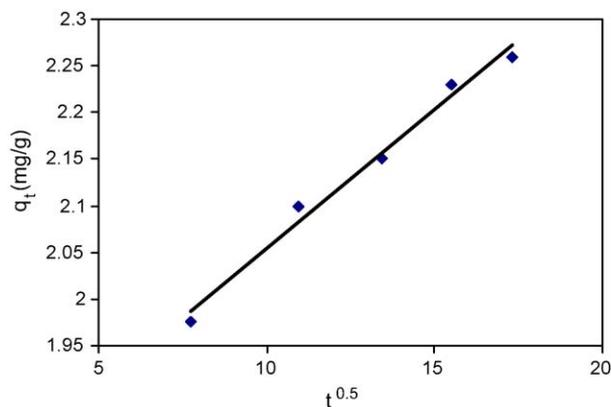


Fig. 13. Mass transfer model [conditions: adsorbent 0.1 g, adsorbate 5 mg l^{-1} , pH 3.5].

Table 4

Adsorbents	Adsorption capacity (mg/g)	pH	C_0 (mg l^{-1})	Reference
Leaf mould	43.1	2	1000	[22]
Coconut shell carbon	10.88	4	25	[22]
Beech sawdust	16.1	1	200	[22]
Sugarcane bagasse	13.4	2	500	[22]
Treated sawdust of Indian Rosewood	10	3	100	[22]
Coconut tree sawdust	3.6	3	20	[22]
Hevea Brasilinesis sawdust activated carbon	44.05	2	200	[22]
Treated sawdust of Sal tree	9.55	3.5	40	Current studies

where q_t is the amount adsorbed at time t (mg/g), t the time (min) and k_{id} is the intra-particle diffusion coefficient ($\text{mg/g min}^{0.5}$).

The k_{id} values were determined from the slope of linear plot between q_t versus $t^{0.5}$ (Fig. 13) and is found to be $0.0298 \text{ mg/g min}^{0.5}$.

7. Conclusion

Treated sawdust has been shown in this paper to be an effective adsorbent for removal of Cr(VI) from aqueous solutions. The optimum adsorption capacity of the treated sawdust was compared with other adsorbents reported in literature (Table 4). The equilibrium time is 3 h for the adsorbent having concentration of 30 mg l^{-1} . The maximum adsorption takes place in the pH range of 4.5–6.0. The adsorption data fitted well to the Langmuir adsorption isotherm and pseudo second order reaction model. Decrease in percentage of adsorption with increase in temperature indicates that the process is exothermic in nature and so low temperatures favor the adsorption process. Due to easy availability and high efficiency for removal of Cr(VI), the treated sawdust is an ideal adsorbent for removal of Cr(VI) from aqueous solutions.

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