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Equilibrium, kinetic and diffusion mechanism of Cr(VI) adsorption onto activated carbon derived from wood apple shell

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Abstract In the present investigation, adsorbent activated charcoal was prepared from wood apple shell by chemical activation and used for Cr(VI) removal from aqueous solutions. Powdered wood apple shell was activated by acid H_2SO_4 and heat treatment in muffle furnace at 600 °C for 2 h. The specific surface area of prepared activated carbon was found to be 1898 $m^2 \, g^{-1}$. Batch adsorption studies reveal that the prepared activated charcoal has a significant capacity for adsorption of Cr(VI) from aqueous solutions. The equilibrium adsorption isotherms investigated in this study include Langmuir and Freundlich at 300 K. The Cr(VI) adsorption was found to be maximum ($>95.0\%$) at pH 1.8. Very small amount of adsorbent activated carbon (1.25 g L^{-1}) could remove $>95.0\%$ Cr(VI) from aqueous solution of initial concentration 75 mg L^{-1}. The Langmuir mono-layer adsorption capacity of Cr(VI) adsorption on activated carbon was found to be 151.51 mg g^{-1}. The dimensionless separation factor (R_L) signifies a favorable adsorption of Cr(VI) on activated charcoal. Adsorption kinetic studies reveal that the adsorption of Cr(VI) onto activated carbon was pseudo-second order chemisorptions and follows film-diffusion as well as intra-particle pore-diffusion mechanism.

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1. Introduction

The adsorbent activated carbon is different from elemental carbon by the oxidation of the carbon atoms found on the outer and inner surfaces. Activated carbons are widely used as adsorbents for the removal of toxic heavy metals, organic pollutants and dyes of environmental concern from air, gases, potable water and wastewater (El-Hendawy, 2003). The activated carbon materials are characterized by their high degree of porosity, incredible large specific surface areas and superficial surface containing functional groups (Jiang et al., 2003) and also possess a high adsorption capacity. Physical and chemical activation methods introduce the surface oxygen functional groups to the carbon. Physical activation methods affect the reaction with hot oxidizing gas such as steam, air, nitrogen and CO_2 at temperatures above 500 °C (Smisek and Cerney, 1970). Chemical activation methods affect the

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reaction between the carbon surface and solutions of oxidizing agents such as sulfuric acid, phosphoric acid, nitric acid, hydrogen peroxide, zinc chloride, potassium permanganate, ammonium persulfate, sodium hydroxide, potassium hydroxide, etc. The phosphoric acid and zinc chloride oxidizing agents are usually used for the activation of lignocellulosic materials. Whereas, to activate precursors like coal or chars usually the potassium hydroxide is used as an oxidizing agent. It has been reported that the activated carbon produced from zinc chloride activation method has a higher specific area than that produced by using phosphoric acid and sulfuric acid activation method (Okada et al., 2003). However, acid activation method is normally popular over zinc chloride activation method because it has bad environmental impact.

Usually activated carbon increases the cost of the treatment process. Due to its economical drawback the interest to enforce cheaper raw materials for the production of activated carbon has incited (Rengarag et al., 2002). Subsequently, a wide variety of agricultural biomass and by-products has been investigated as precursors for the production of activated carbon in addition to wood and coal. The choice of a cheap precursor waste biomass reduces the production cost of activated carbon.

In biosphere chromium exists only in two stable oxidation states, such as trivalent and hexavalent. Relatively the hexavalent chromium, Cr(VI) is more toxic than trivalent, Cr(III) due to its carcinogenic, mutagenic and teratogenic properties. Many industries release large quantities of wastewater containing heavy metals above the permissible limit and it is well known that some metals can have toxic harmful effects on many forms of life (Murathan and Benli, 2004; Akar and Malkoc, 2004). Cr(VI) enters into the aquatic environment from cement, chromate preparation, electroplating, metal finishing, tannery and fertilizer industries (Heidmann and Calmano, 2008). Particularly leather industry generates a large quantity of polluting wastewater from the tanning of animal skins and hides, which contain chromium above the permissible limit (Golder et al., 2007). In last few decades, the removal of toxic metal Cr(VI) ions from industrial wastewater is a widely and important studied research area. The Ministry of Environment and Forests (MOEF), Indian Government's has set Minimal National Standards (MINAS) of 2.0 mg/L for industries, to safe discharge of effluents containing chromium metal ions into surface waters (Yoganarsimhan, 2000). The World Health Organization (WHO) has set the maximum permissible level of 0.05 mg/L for chromium in drinking water.

In present study, the activated carbon was prepared by chemical activation followed by heat treatment from agricultural waste biomass of wood apple shell. The adsorption isotherms, kinetic and diffusion mechanism were investigated. The citrus fruit wood apples were used as Rejuvenators, monotype genus *Limonia acidissima* L found in Asian countries, especially in Indian subcontinent. Locally it is known as kapitha, kaith or wood apple. Pulp of fruit is mixed with sugar and taken to cure diarrhea and dysentery. The *Limonia acidissima* plants are more commonly found in Thane district of Maharashtra, S. Chnad district of Madhya Pradesh in India ((Yoganarsimhan, 2000) and also found in dry lands throughout India.

2. Materials and methods

2.1. Preparation and characterization of adsorbent

The activated carbon was prepared from agricultural waste biomass, the hard shell of wood apple fruit. The shells were broken down to smaller pieces and soaked in concentrated H_2SO_4 (98%) at 1:1 (W:V) ratio for 48 h. Further, it was activated in muffle furnace for 2 h at 600 °C and cooled at room temperature. The activated carbon was repeatedly washed several times with distilled water until the wash water pH became that of the distilled water (nearly 7). The carbon obtained was dried at 50 °C in an oven for overnight to remove the moisture and stored in desiccators. The prepared carbon was used as an adsorbent for the removal of Cr(VI) from aqueous solutions.

The prepared activated carbon was characterized by FTIR analysis and the pH at zero point charge (pH_{pzc}) onto the surface of activated carbon was determined by batch equilibrium method (Lazareví c et al., 2007). Initial pH values (pH_i) of 25 mL of KNO_3 solutions (0.1 M) were adjusted in pH range of 2–8 using 0.1 M HCl or 0.1 M NaOH solution. Then, 0.1 g of wood apple shell activated carbon was added to each sample. Equilibration was carried out by shaking, in a thermostated magnetic shaker for 24 h (greater than equilibrium contact time) at 298 K. The dispersions were then filtered and the final pH of the solutions (pH_f) was measured. The pH at point of zero charge (pH_{pzc}) was found from a plot of (pH_i-pH_f) versus pH_i. The surface area of prepared activated carbon was determined, based on maximum monolayer adsorption capacity (q_{max}) of methylene blue calculated from Langmuir isotherm model. The specific surface area (S_A) of prepared activated carbon ($m^2 \, g^{-1}$) was obtained by the equation (Baraka et al., 2006):

$$S_A = \frac{6.023 \times 10^{23} \times A_0 \times q_{max}}{1000 \times M} \quad (1)$$

The value of occupied surface area (A_o) of one molecule of methylene blue is 197.2 $Å^2$ (Graham, 1955). M is the molecular weight of methylene blue.

2.2. Preparation of Cr(VI) solutions

Stock solution of Cr(VI) was prepared (1000 mg L^{-1}) by dissolving the desired quantity A. R. Grade potassium dichromate ($K_2Cr_2O_7$) in double distilled water. The sample solutions of concentrations range from 25 to 200 mg L^{-1} were prepared by diluting the stock solution to the desired concentrations.

2.3. Adsorption experiments

In the determination of adsorption equilibrium isotherm batch studies, 0.05 g of activated carbon derived from wood apple shell and 40 mL of Cr(VI) solutions (75–200 mg L^{-1}) were transferred in a conical flask, and shaken on a thermo-stated magnetic stirrer at 300 K for 120 min (the time required for equilibrium to be reached). The predetermined optimum pH 1.8 of the solutions was adjusted with 0.01 M HCl or 0.01 M NaOH solution by using a pH-meter (Systronic). The concen-
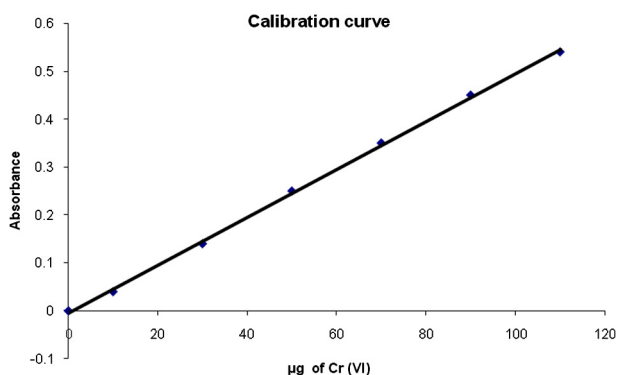
Figure 1 Calibration curve for estimation of un-adsorbed Cr(VI) in aqueous solutions.

tration of un-adsorbed Cr(VI) in aqueous solution was determined by 1, 5-diphenyl carbazide method (APHA, 1999). A calibration graph of absorbance versus known concentrations of Cr(VI) was obtained using spectrophotometer (Systronic) at λ_{max} 540 nm (Fig. 1). Removal efficiency of Cr(VI) and the amount of Cr(VI) adsorbed at equilibrium, q_e (mg g^{-1}), were calculated by the equation 2 and 3, respectively:

$$\%Cr(VI) \text{ removal} = \frac{Co - Ce}{Co} \times 100 \qquad (2)$$

where C_o (mg L^{-1}) and C_e (mg L^{-1}) are initial and equilibrium concentrations of Cr(VI) in aqueous solutions, respectively.

$$q_e = \frac{C_o - C_e}{M} \times V \qquad (3)$$

where V is the volume of Cr(VI) solution (L), M is the mass of wood apple shell activated charcoal used (g). Further, the data were analyzed to study equilibrium adsorption isotherms include Langmuir and Freundlich isotherms at 300 K.

Further, to investigate adsorption kinetic experiments, batch adsorptions were conducted by shaking 0.05 g of activated carbon derived from wood apple shell and 40 mL of Cr(VI) solutions (25–100 mg L^{-1}) was transferred in a conical flask, and shaken on a thermo-stated magnetic stirrer at 300 K for preset time interval of 10 min up to 80 min. All the mixtures after adsorption operation were centrifuged and the Cr(VI) concentration in the supernatant was estimated by diphenyl carbazide method.

The amount of Cr(VI) adsorbed at time t (min), q_t (mg g^{-1}), was calculated from the following equation:

$$q_t = \frac{C_o - C_f}{M} \times V \qquad (4)$$

where V is the volume of Cr(VI) solution (L), M is the mass of activated charcoal (g).

3. Result and discussions

3.1. Characteristics of the prepared activated carbon

The FTIR spectrum of prepared activated carbon from wood apple shell shows functional groups that are shown in Table 1, it reveals that the most abundant functional groups found onto the prepared activated carbon include aromatic (C–H), carboxylic acid (C–O, C=O and O–H), carbonyl (C=O), alkane (C–H) and amine (N–H, C–N). This suggest to adsorb Cr(VI) onto prepared activated carbon some of these functional groups are responsible. It was found that the pH at point of zero charge (pH$_{pzc}$) of the activated carbon was 3.95 (fig. 2). The activated carbon prepared from wood apple shell exhibits a relationship between pH$_{pzc}$ and adsorption capacity of the adsorbent used. The result shows that cation adsorption is favorable at pH value higher than point of zero charge, while anion adsorption is favored at pH values lower than point of zero charge (Nomanbhay and Palanisamy, 2005). This investigates that the pH less than 3.95 adsorption of Cr(VI) is more favorable, due to strong electrostatic attraction between anionic HCrO$_4^-$ with protonated oxygen containing surface functional group onto activated charcoal. The specific surface area of activated carbon was found to be 1898 m^2 g^{-1}.

3.2. Effect of pH

The pH of the aqueous solution is an important parameter for the adsorption of both anions and cations at the liquid–solid interface. The effect of pH on Cr(VI) adsorption onto the activated carbon prepared from wood apple shell was found that the adsorption of Cr(VI) increased from 40% to greater than 95% with a decrease in pH from 7 to 1. The results show that Cr(VI) adsorption is strongly pH dependent. The pH dependency is both related to the surface properties of the activated carbon and chromium species in solution (Jain et al., 2009). The Cr(VI) species may be represented in various forms, such

Table 1 Functional groups on activated carbon prepared from wood apple shell by FTIR analysis.

| IR frequency (cm^{-1})	Type of vibration	Functional group
3070.78	C–H stretching	Aromatic
2806.52	C–H stretching	Alkanes
1768.78	C=O stretching	Carbonyl
1610.61	N–H bending	Primary amine
1508.38	C–C stretching	Aromatic
1330.93	C–N stretching	Aromatic amine
1319.35	C–O stretching	Carboxylic acid, ester, ether
1109.11	C–O stretching	Carboxylic acid, ester, ether
1060.88	C–O stretching	Carboxylic acid, ester, ether
952.87	O–H bending	Carboxylic acid
896.93	C–H bending	Aromatic
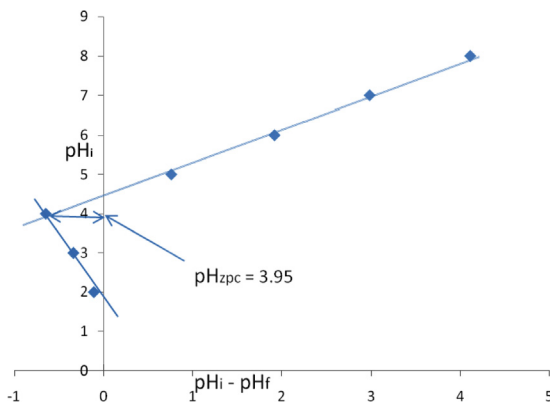
Figure 2 Determination of pH at zero point charge (pH_{pzc}) on surface of prepared activated carbon.

Figure 4 Langmuir isotherm of Cr(VI) adsorption onto activated carbon at 300 K.
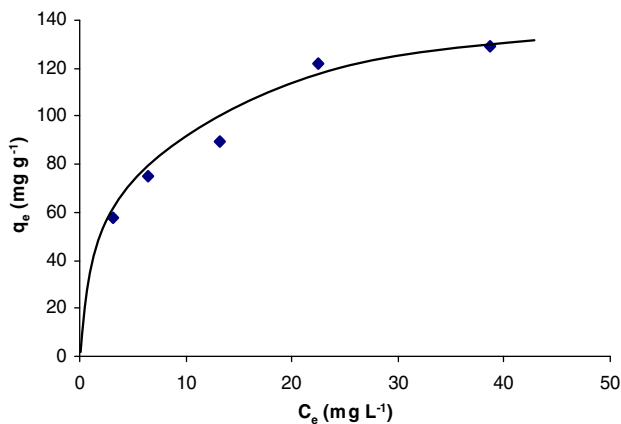

Figure 3 Adsorption isotherm of Cr(VI) adsorption onto activated carbon at 300 K.

as H_2CrO_4, $HCrO_4^-$, CrO_4^{2-} and $Cr_2O_7^{2-}$ in the solution phase as a function of pH. The anionic form of hexavalent chromium $HCrO_4^-$ is more dominant in acidic pH.

The value of zero point charge (pH$_{pzc}$) on the surface of prepared activated carbon was found to be 3.95 (Fig. 2). The maximum adsorption capacity of Cr(VI) below the pH at zero point charge can be explained by species of chromium and the adsorbent surface. There was strong electrostatic attraction between $HCrO_4^-$ species with protonated active site $[Ar–OH_2]^+$ of adsorbent surface in acidic condition as:

$$[Ar - OH_2]^+ + HCrO_4^- \rightarrow ArHCrO_4 + H_2O, pH < 3.95 \quad (5)$$

where $[Ar–OH_2]^+$ is one of the representative protonated active functional group on adsorbent surface of prepared activated carbon. As the pH is increased above the zero point charge, there was a reduction in electrostatic attraction between Cr(VI) species and the surface of activated carbon. Hence, the adsorption was more favored below the pH at zero point charge.

3.3. Adsorption isotherms

In the present research, the adsorption equilibrium data of Cr(VI) on activated carbon prepared from wood apple shell
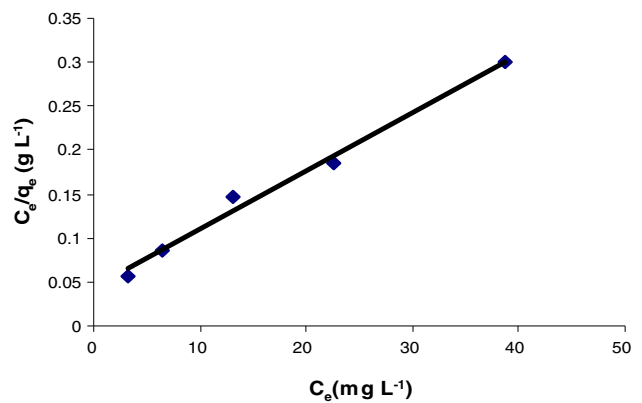
were analyzed in terms of two common Langmuir and Freundlich isotherm models.

The equilibrium adsorption isotherm aims to how the adsorbate molecules or ions are distributed between the solid adsorbent and the liquid solutions. To discover by searching out the suitable isotherm model, analysis of isotherm data by correcting to different isotherm models is a worthy step that can be used to design the adsorption purpose. Fig. 3 shows a typical equilibrium adsorption of Cr(VI) onto prepared activated carbon at 300 K. The adsorption isotherm curve rises steeply at lower concentrations of Cr(VI) and approaches to a plateau at higher concentrations.

Based on ideal assumption of a monolayer adsorption of adsorbate on adsorbent surface the Langmuir isotherm model (Langmuir, 1918) is expressed in linear form as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (6)$$

where, q_m is the maximum monolayer adsorption capacity (mg g^{-1}), and K_L is the Langmuir constant which is related to the heat of adsorption (L mg^{-1}). The pH of Cr(VI) solution after adsorption was maintained in between 1.8 and 2.2 and estimated using digital pH-meter. The pH value should be maintained due to that, the chelating agents will complex Cr(VI) only in that pH range. The constants q_m and K_L are determined by plotting the specific sorption, C_e/q_e versus equilibrium sorption; C_e (Fig. 4) and listed in Table 2.

The essential features of Langmuir isotherm dimensionless separation factor (R_L) are given by the Eq. (7) as (Hall et al. 1966):

$$R_L = \frac{1}{1 + K_L C_0} \quad (7)$$

The value of separation factor R_L indicates either the adsorption isotherm to be unfavorable ($R_L > 1$), favorable ($0 < R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). The calculated R_L values at different initial concentrations of Cr(VI) are in the range from 0.0318 to 0.0805 in all experimental systems shown in Table 2, which confirms the favorable uptake process of chromium adsorption. Lower R_L values at all initial concentrations of Cr(VI) showed that the adsorption was more favorable at concentration range of 75–200 mg L^{-1}.

Table 2 Adsorption isotherm parameters and correlation coefficients calculated for Langmuir and Freundlich adsorption models at 300 K for Cr(VI) adsorption onto activated carbon.

Isotherms	Constant parameters at 300 K			
	q_{max} (mg g^{-1})	K_L (L mg^{-1})	R_L	R^2
Langmuir	151.51	0.1524	0.0805 (75 mg L^{-1})	0.9883
			0.0616 (100 mg L^{-1})	
			0.0499 (125 mg L^{-1})	
			0.0361 (175 mg L^{-1})	
			0.0318 (200 mg L^{-1})	
Freundlich		1/n	K_F [(mg g^{-1})(mg^{-1})$^{1/n}$]	R^2
		0.3389	39.07	0.9753

Table 3 Comparisons of Langmuir monolayer adsorption capacity, q_m of various activated carbons derived from waste biomass.

Adsorbents	Monolayer adsorption capacity, q_m (mg g^{-1})	References
Fir wood activated charcoal	180.3	(Khezami and Capart, 2005)
Green alga activated carbon	112.36	(El-Sikaily et al. 2007)
Tires activated carbon	5850	(Hamadi et al. 2001)
Hazelnut shell activated carbon	52.2	(Selvi et al. 2001)
Rubber wood sawdust activated carbon	44.05	(Karthikeyan et al. 2005)
Coconut shell carbon	2000	(Alaerts et al. 1989)
Coconut shell carbon	1088	(Babel and Kurniawan, 2000)
Wood apple shell activated carbon	151.51	Present study
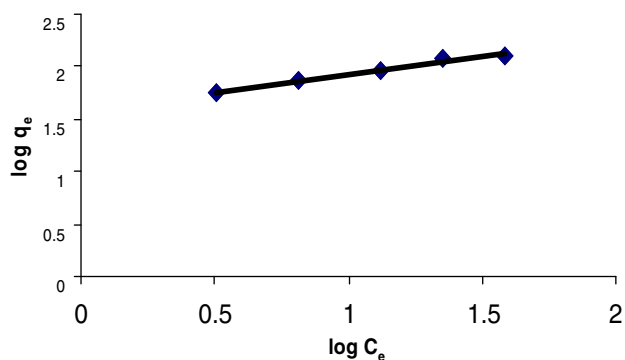
Figure 5 Freundlich isotherm of Cr(VI) adsorption onto activated carbon at 300 K.

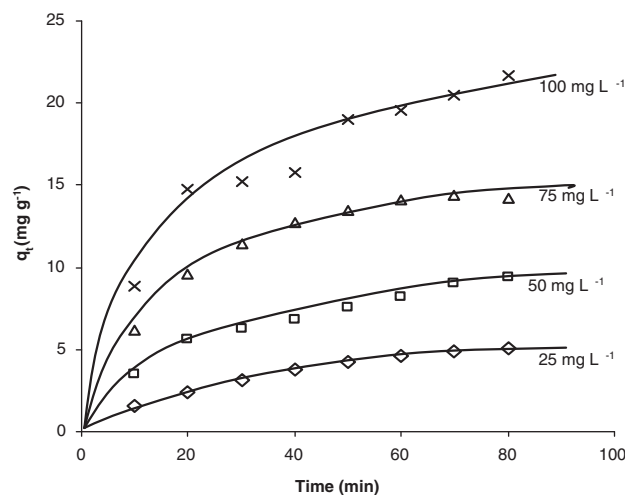**Figure 6** Adsorption kinetics of Cr(VI) onto activated carbon at different concentrations.

The comparison of Cr(VI) monolayer adsorption capacities (q_m) by various activated carbons derived from agricultural biomasses is summarized in Table 3. The activated carbon used in this research showed higher adsorption capacity compared with other activated carbons. Thus the utilization of wood apple shell for the preparation of activated carbon for Cr(VI) removal from aqueous solutions shows promising future.

The Freundlich adsorption isotherm model (Freundlich, 1906) is expressed by equation as:

$$q_e = K_F C_e^{1/n} \qquad (8)$$

The linear logarithmic form of the Freundlich equation is expressed by

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (9)$$

where, K_F (mg$^{1-1/n}$ g^{-1} L$^{1/n}$) and 1/n are the Freundlich constants. The plot of $\log q_e$ versus $\log C_e$ (Fig. 5) enables the determination of isotherm constants K_F and 1/n (Table 2).

The experimental isotherm parameters along with regression coefficient are listed in Table 2. The adsorption isotherms based on parameter values are compared with experimental data at 300 K. High R^2 values (> 0.97) compared to the Freundlich model indicate that the adsorption of Cr(VI) onto activated carbon derived from wood apple shell follows the Langmuir isotherm model.

Table 4 Kinetic parameters for Cr(VI) adsorption onto activated carbon derived from wood apple shell at different concentrations.

Initial Conc. of Cr(VI) (C_o) (mg L^{-1})	$q_{e,exp}$ (mg g^{-1})	Pseudo-first order kinetic			Pseudo-second order kinetic			
		$q_{e,cal}$ (mg g^{-1})	k_1 (min^{-1})	R^2	$q_{e,cal}$ (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	h_o (mg g^{-1} min^{-1})	R^2
25	7.35	6.39	0.0115	0.986	7.94	0.00288	0.1815	0.994
50	11.58	9.29	0.0231	0.986	12.19	0.00302	0.4502	0.983
75	17.25	11.07	0.0184	0.916	17.86	0.00327	1.044	0.995
100	26.68	19.01	0.0231	0.959	27.03	0.00177	1.292	0.982

3.4. Adsorption kinetics

In order to further understand the adsorption process of Cr(VI) onto activated carbon kinetic investigation was conducted. Lagergren Pseudo-first order, Ho and Mckay pseudo-second order kinetic models have been used for all experimental data. The plot q_t versus t (Fig. 6) at different concentrations of Cr(VI) gives a typical adsorption kinetic of adsorption. The Fig. 6 shows that the adsorption process can be divided into two steps, the rapid 70% to 80% uptake of Cr(VI) was observed within first 30–35 min and slow uptake of Cr(VI) observed until equilibrium was reached.

The pseudo-first order model (Lagergren, 1898) was widely used for the adsorption of liquid adsorbate on solid adsorbent on the basis of adsorption capacity at different time intervals.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{10}$$

where q_e and q_t are the adsorption capacity at equilibrium and at time t (mg g^{-1}), respectively, k_1 is the pseudo-first order rate constant of adsorption (min^{-1}). After integration and applying boundary conditions t = 0 to t = t and qt = 0 to qt = qt, to the Eq. (10) becomes to linear form as:

$$\log(q_e - q_t) = \log q_e - \frac{k1}{2.303} \times t \tag{11}$$

Plotting $\log(q_e - q_t)$ versus t, the constants k_1 (min^{-1}) and q_e (mg g^{-1}) were determined and listed in Table 4. The experimental data, q_e, exp differ from theoretical values (q_e, cal) (Table 4), suggests that the adsorption of Cr(VI) on activated carbon does not follow entirely the pseudo-first order adsorption kinetics.

The pseudo-second order model (Ho and McKay, 1998) is based on certain assumption that the adsorption of adsorbate onto adsorbent supports second order chemisorptions.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{12}$$

where k_2 is the pseudo-second order rate constant of adsorption (g mg^{-1} min^{-1}).

For the boundary conditions t = 0 to t = t and qt = 0 to qt = qt, the integrated form of Eq. (12) becomes:

$$\frac{1}{q_e - qt} = \frac{1}{q_e} + k_2 \, t \tag{13}$$

This is the integrated rate law for pseudo-second order chemisorptions reaction, Eq. (13) can be rearranged to obtain Eq. (14).

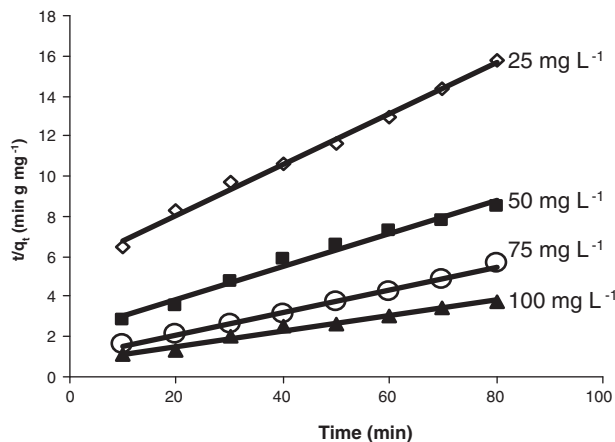$$\frac{t}{q_t} = \frac{1}{h_o} + \frac{1}{q_e} \times t \tag{14}$$

Figure 7 Pseudo-second order plot at different concentrations of Cr(VI) adsorption on activated carbon.

By plotting a curve of t/q_t versus t, the constants q_e and initial rate of adsorption, h_o (mg g^{-1} min^{-1}) can be evaluated. The initial rate of adsorption is also related as (Ho, 2003):

$$h_o = k_2 q_e^2 \tag{15}$$

The values of q_e, and h_0 were used to evaluate the value of pseudo-second order rate constant, k_2. The values of q_e, h_0, k_2 and R^2 are listed in Table 4. The plot of t/q_t versus t gives an excellent straight line relation for adsorption of Cr(VI) on activated carbon (Fig. 7). There was only little difference between q_e, exp and q_e, cal and R^2 values are greater than 0.982 (Table 4) for all experimental concentrations of Cr(VI), confirming the applicability of the pseudo-second order kinetic for the adsorption process. It can also be seen in Table 4 that with an increase in initial metal concentration the initial rate of adsorption (h_o) increases, whereas the rate constant of adsorption (k_2) is fairly constant.

3.5. Adsorption diffusion mechanisms

To realize the exact diffusion mechanism, the adsorption kinetic data were further analyzed by an intra-particle diffusion model (Weber and Morris, 1963):

$$q_t = k_d t^{1/2} + I \tag{16}$$

where k_d is the intra-particle diffusion rate constant (mg g^{-1} min$^{-1/2}$), and I is a constant that gives idea about the boundary layer thickness (mg g^{-1}). According to this model, if the plot of q_t versus $t^{1/2}$ gives a straight line, then the adsorption process is controlled by intra-particle diffusion
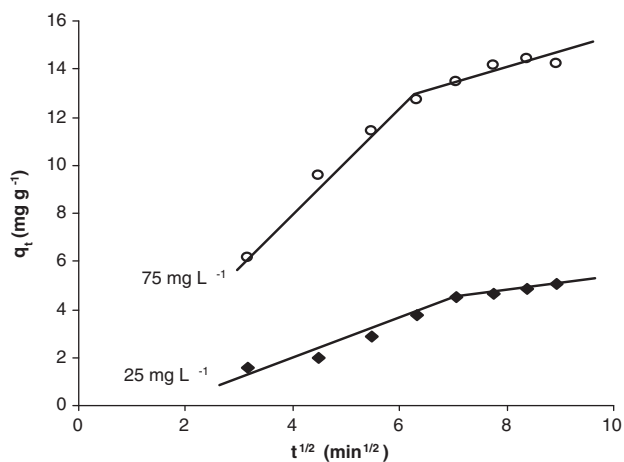
Figure 8 Intra-particle diffusion plot of Cr(VI) (25 and 75 mg L^{-1}) adsorption onto activated carbon.

Figure 10 Adsorption plot of pore diffusion mechanism of different concentrations of Cr(VI) onto activated carbon.
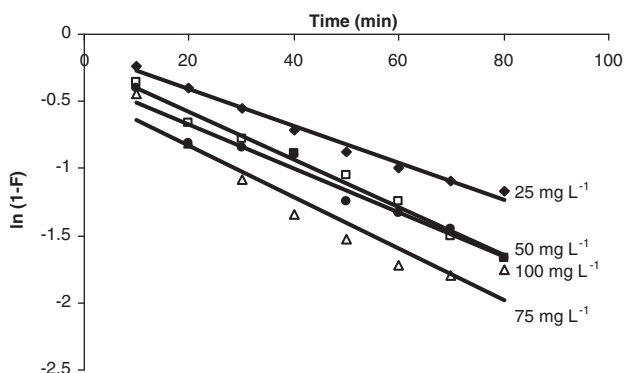

Figure 9 Adsorption plot of film diffusion mechanism of different concentrations of Cr(VI) onto activated carbon.

and if the data exhibit multi-linear plots, then two or more steps control the adsorption process (Saha, 2010). In the present research, the plots present two distant linear portions (Fig. 8), indicating adsorption was not controlled by only intra-particle diffusion. The first linear portion was due to the external surface adsorption in which uptake rate of chromium ions was high due to the film diffusion of Cr(VI) through solution onto the external surface of activated carbon. The later gradual linear portion refers to slow intra-particle pore diffusion. This indicates that both external film and intra-
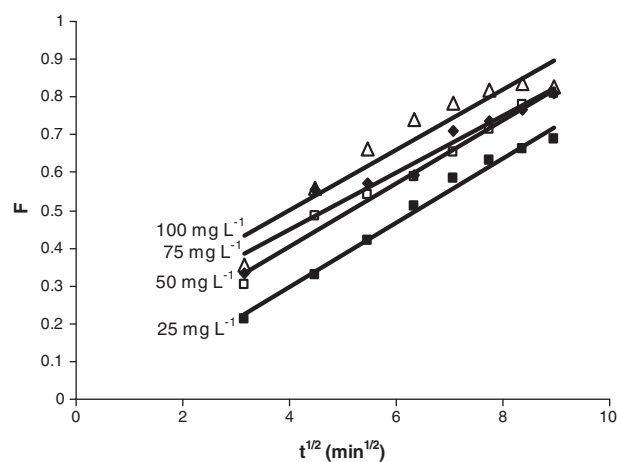
particle pore diffusion mechanism was involved in the Cr(VI) adsorption onto activated carbon.

Further, to evaluate the diffusion mechanism quantitatively, a model based on Fick's law was applied. It is known that the mechanism of metal ion adsorption can be explained either by film diffusion or pore diffusion (Niboua et al., 2010).

The film diffusion mechanism is expressed by equation:

$$\ln(1 - F) = \ln\left(\frac{6}{\pi^2}\right) - \left(\frac{D_i}{r_o^2}\right).\pi^2.t \tag{17}$$

where D_i is the film diffusion coefficient (cm^2 s^{-1}), F is the fraction of amount adsorbed at time t to amount adsorbed at equilibrium time, i.e. q_t/q_e, r_o is the radius of adsorbent particles (0.866×10^{-3} cm) assumed to be spherical. The values of film diffusion coefficient were determined from the slope (S_i) of linear plots of ln (1−F) versus t (min) (Fig. 9).

$$D_i = -\frac{S_i.r_o^2}{\pi^2} \tag{18}$$

The calculated values of film diffusion coefficient, D_i at different concentrations for Cr(VI) ions are presented in Table 5.

The linear form of pore diffusion mechanism equation, assumes a particle diffusion to be rate-limiting steps, is expressed as:

$$F = \frac{6}{r_o}\left(-\frac{D_{ii}.t}{\pi}\right)^{1/2} \tag{19}$$

The pore diffusion coefficients, D_{ii} are obtained from the slope (S_{ii}) of the linear plots of F versus $t^{1/2}$ (Fig. 10).

Table 5 Adsorption mechanism kinetic parameters for Cr(VI) adsorption onto activated carbon derived from wood apple shell at different concentrations.

Initial concentration of Cr(VI) C_o (mg L^{-1})	Diffusion coefficient (cm^2 s^{-1})	
	Film diffusion ($\times 10^{-9}$)	Pore diffusion ($\times 10^{-12}$)
25	0.988	10.7
50	1.29	9.74
75	1.44	8.41
100	1.22	6.49

$$D_{ii} = \frac{S_{ii}^2 \pi r_o^2}{36} \tag{20}$$

The calculated values of pore diffusion coefficient, D_{ii} at different concentrations for Cr(VI) ions are presented in Table 5. If the values of film diffusion coefficient are in the range of 10^{-6}–$10^{-8} \, cm^2 \, sec^{-1}$ (Michelson et al., 1975), then the adsorption mechanism is controlled by film diffusion mechanism. While, the values of pore diffusion coefficient lie in the range of 10^{-11}–$10^{-13} \, cm^2 \, s^{-1}$ (Mckay and Poots, 1980), then the adsorption mechanism is controlled by pore diffusion mechanism.

In the present study, experimental analyzed data reveal that the values of film and pore diffusion coefficients are in the order of 10^{-9} and $10^{-12} \, cm^2 \, s^{-1}$, respectively which indicates that the adsorption of Cr(VI) onto activated carbon derived from wood apple shell was controlled by both film and pore diffusion mechanism.

4. Conclusions

The present study investigated the removal of Cr(VI) from aqueous solution onto activated carbon derived from wood apple shell. The removal efficiency of Cr(VI) was greater than 95% at pH 1.8 and very low amount $1.25 \, g \, L^{-1}$ of activated carbon. The adsorption process followed the Langmuir isotherm model better as compared to Freundlich isotherm. The Langmuir monolayer adsorption capacity of Cr(VI) onto prepared activated carbon was $151.51 \, mg \, g^{-1}$ at 300 K. The adsorption kinetic reveals that the pseudo-second order model fitted very well to the adsorption of Cr(VI) onto activated carbon, indicates that the adsorption process follows chemisorption. Intra-particle diffusion model analysis suggests that adsorption of Cr(VI) onto activated carbon was controlled by both film as well as pore diffusion mechanism. The investigation shows that the agricultural waste biomass wood apple shell can be effectively utilized for the preparation of activated carbon and become a promising adsorbent for the removal of Cr(VI) from aqueous solutions.

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