

## Thermodynamic and Kinetic Studies of Chromium (VI) Adsorption by Sawdust Activated Carbon

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**Summary:** Low cost activated carbon, prepared from saw dust of *Ziziphus jujube* by chemical activation with phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) was characterized and utilized for the removal of Cr (VI) ions from aqueous solutions under different conditions of solution pH, contact time, initial concentration, carbon dose and temperature. Adsorption of Cr (VI) ions was found highly pH dependent that increased with decrease in solution pH. The removal of Cr (VI) ions increased with increase in temperature, initial concentration and contact time until equilibrium was established. Langmuir's adsorption isotherm model and pseudo - second order kinetic equation were found better fitted to describe the experimental data. Thermodynamic study revealed the feasibility, spontaneity and endothermic nature of the adsorption process. The used carbon was regenerated by treating with HCl solution. In comparison to other adsorbents, the results indicated that the prepared saw dust activated carbon could be an eco-environment friendly and efficient adsorbent for removal of Cr (VI) ions from aqueous solutions.

**Keywords:** Activated carbon; *Ziziphus jujube*; Adsorption isotherm; Chromium (VI); Thermodynamic; Kinetics

### Introduction

Heavy metals are potential water pollutants due to their toxic and non-biodegradable nature that pose a severe threat to public health and the environment. Among heavy metals, Cr (VI) is one of the most hazardous pollutants due to its smaller size, stability and solubility in water. It causes cancer in digestive tract and lungs as well as a number of other diseases. Depending on pH of the aqueous system, Cr (VI) may exist in different forms such as CrO<sub>4</sub><sup>-2</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>-2</sup>, HCrO<sub>4</sub><sup>-1</sup>, Cr<sub>3</sub>O<sub>10</sub><sup>-2</sup> and Cr<sub>4</sub>O<sub>13</sub><sup>-2</sup> etc in aqueous solution. In natural waters, the Cr (VI) may exist most commonly as Cr<sub>2</sub>O<sub>7</sub><sup>-2</sup> and HCrO<sub>4</sub><sup>-1</sup> which are soluble and mobile in water. The main sources of natural waters contamination with toxic Cr (VI) ions are industrial discharges from paints, pigments, photography, textile dyeing, mining, wood preservation, alloying, chrome plating, leather tanning, etc. The World Health Organization (WHO) permissible limit of Cr (VI) ions in drinking water is 0.05 mg/L and in inland water is 1.0 mg/L. Due to its toxic and harmful effects on the living organisms and the environment, the removal of Cr (VI) ions from potable and waste waters by eco-friendly methods is of primary importance [1-5].

The removal of heavy metal ions from aqueous solutions by adsorption on porous solid adsorbents is an efficient, cost effective and environment friendly method. Different adsorbents can be utilized for the removal of various pollutants from aqueous phase and other media; however,

activated carbons are the most widely used adsorbents due to their characteristic porosity, surface area, better reactivity and surface chemistry. The adsorption properties of activated carbons depend upon the nature of starting materials, nature of surface functional groups, surface area, conditions of adsorption and nature of adsorbates, etc. Large variety of carbonaceous materials can be used for the production of activated carbons but the commercial activated carbons are expensive due to the use of non-renewable and relatively expensive starting materials. The use of cheaper and abundantly available agricultural by-products/wastes as precursors for carbon adsorbents is increasing worldwide due to their low ash contents and desirable hardness. The adsorption capacities of such activated carbons have been found comparable and in many cases even better than those of commercial carbons. Many studies have been reported the utilization of activated carbons derived from agricultural by-products/wastes such as sugarcane bagasse, corn cobs, rice straw, hazelnut shells, dates' stones, nutshells, etc [6-9].

*Ziziphus jujube* (Ber) plants grow in Pakistan abundantly and their wood is used in furniture or as fuel. A huge volume of saw dust of these plants is produced at the saw mills that is neither disposed off properly nor utilized as valuable commodity. Such large scale production of the saw

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dust and lack of proper disposal management may result in several environmental problems. The conversion of saw dust into activated carbon for the removal of toxic pollutants from aqueous solutions is of great importance from environmental and economic point of view. Up to our knowledge, very little work has been reported regarding the use of Ber plants and their by-products for preparation of activated carbons [10]. The present study included the preparation of activated carbon from saw dust of *Ziziphus jujube* plants by chemical activation with phosphoric acid ( $H_3PO_4$ ) and its use for the removal of Cr (VI) ions from aqueous solutions. Equilibrium, thermodynamic and kinetic studies of Cr (VI) ions adsorption by the prepared activated carbon were performed to evaluate the adsorption capacity of the prepared carbon sample as well as to investigate the feasibility and nature of adsorption.

## Results and Discussion

### Characterization

Characterization of activated carbon sample is of great importance in order to explain the mechanism and behavior of adsorption as well as the adsorption capacity. The prepared activated carbon sample was characterized by determination of pH, PZC, surface area, surface functional groups and pore-volumes etc, as shown in Table-1. It can be seen from the table that the prepared sample has relatively lower pH, PZC and BJH surface area while sufficient BET surface area and pore-volumes. The lower pH and PZC could be attributed to the presence of acidic functional groups in the form of lactonic, phenolic and carboxylic functional groups on the surface of activated carbon. The higher BET and lower BJH surface area indicated that the prepared carbon is microporous in nature. The strong chemical interaction of the activating agent ( $H_3PO_4$ ) with the precursor material during soaking and the evolution of volatile matter could be accounted for larger BET surface area and larger pore-volumes [11-13].

Table-1: Characteristic parameters of the prepared activated carbon.

1	pH	4.83
2	PZC	4.91
3	Surface area ( $S_{BET}$ ), $m^2/g$	445
4	Surface area ( $S_{BJH}$ ), $m^2/g$	23.35
5	Micro-pore volume ( $cc/g$ )	0.22
6	Total pore volume ( $cc\ g^{-1}$ )	0.24
7	Meso-pore volume ( $cc/g$ )	0.02
8	Average pore radius ( $A^{\circ}$ )	11.22
9	Carbonyl ( $m.mol.g^{-1}$ )	0
10	Phenolics + lactonics $\times 10^{-3}$ ( $m.mol.g^{-1}$ )	2.32
11	Carboxylics $\times 10^{-3}$ ( $m.mol.g^{-1}$ )	1.8
12	Quinone $\times 10^{-3}$ ( $m.mol.g^{-1}$ )	3.98
13	Basic groups $\times 10^{-3}$ ( $m.mol.g^{-1}$ )	1.06

### Adsorption Studies of Cr (VI) Ions

#### Effect of Solution pH

pH of solution is an important parameter that determines the charge on adsorbent surface, extent of ionization and speciation of metal adsorbate, hence the nature of interactions between an adsorbent and metal adsorbate. Fig. 1 shows the effect of pH on Cr (VI) ions adsorption. It can be observed from the Fig that maximum adsorption of Cr (VI) ions was found at pH 2 which decreased with increase in solution pH. The change in adsorption capacity could be attributed to the change in the anionic state of Cr (VI) and surface properties of carbon with change in solution pH. At pH 1, Cr (VI) exists as  $H_2CrO_4$  while in the pH range of 1 – 6, it may exist in different anionic forms like  $CrO_4^{-2}$ ,  $Cr_2O_7^{-2}$ ,  $HCrO_4^{-1}$ ,  $Cr_3O_{10}^{-2}$  and  $Cr_4O_{13}^{-2}$ . At pH 2 – 6, the common forms of Cr (VI) are considered to be hydrogen chromate ( $HCrO_4^{-1}$ ) and dichromate ( $Cr_2O_7^{-2}$ ) while chromate ( $CrO_4^{-2}$ ) is expected at pH higher than 6. The most common and dominant form of Cr (VI) in aqueous solution up to pH 5 is  $HCrO_4^{-1}$ [3-5]. At lower pH 2, the increased electrostatic attraction b/w highly protonated positive surface of carbon and negatively charged hydrogen chromate ( $HCrO_4^{-1}$ ) anions might be responsible for the maximum adsorption. As pH increases, the concentration of  $H^+$  ions decreases while  $OH^{-1}$  ions increases which makes the carbon surface less and less positively charged. The decreased adsorption of Cr (VI) ions could be attributed to the reduced affinity of hydrogen chromate anions and their competition with  $OH^{-1}$  ions for the carbon surface. Indeed, an increase in solution pH was noted after adsorption that was obviously due to the increased concentration of  $OH^{-1}$  ions. Keeping in mind the pH of natural waters, pH 4 was selected as optimum pH and all subsequent experiments were performed at this pH. Many other researchers have reported similar results [13-19].

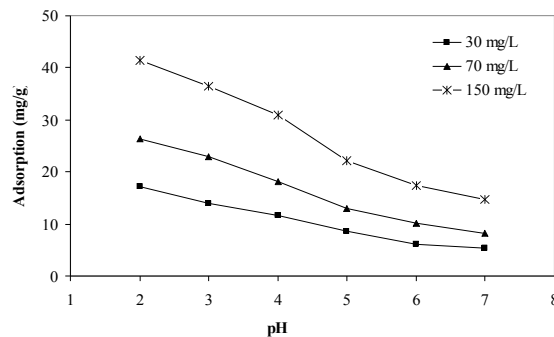


Fig. 1: Effect of pH on Cr (VI) adsorption by activated carbon.

(Carbon dose = 0.1g, shaking speed = 110rpm, T = 298K, volume of solution taken: 40 mL)

*Effect of Contact Time and Initial Concentration*

The effect of contact time on the removal of Cr (VI) ions from aqueous solution of initial concentration 30, 70 and 150 mg/L by adsorption on the prepared activated carbon sample is shown in Fig. 2. The Fig shows that the adsorption of Cr (VI) ions increased with increase in contact time and become almost constant after the equilibrium time of 300 minutes. Adsorption was very rapid in the early 60 minutes which then become decreased and almost constant after 300 minutes. The higher adsorption of Cr (VI) ions observed in the early stages could be attributed to the larger surface area of the adsorbent available for adsorption. When the adsorbent surface becomes covered due to monolayer formation of the adsorbed ions, the rate of adsorption decreased due to the slow pore diffusion of ions into the bulk of the adsorbent. It can also be observed from Fig. 2 that the amount of Cr (VI) ions adsorbed increased with increase in initial concentration. The increase in the amount of Cr (VI) ions adsorbed from solution of higher initial concentrations might be due to covering of all the active sites of adsorbent surface by the larger number of Cr (VI) ions in solution. [15-16].

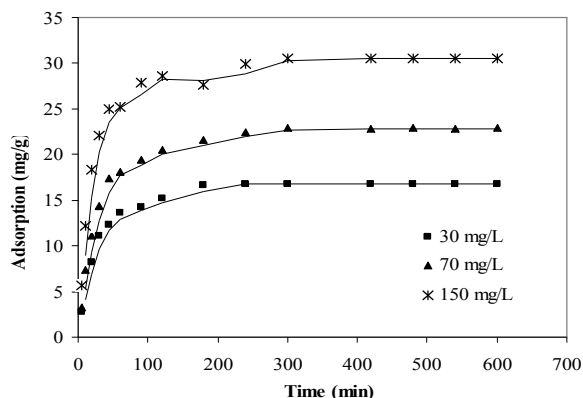


Fig. 2: Effect of contact time and Initial concentration on Cr (VI) adsorption.

(Carbon dose = 0.1g, shaking speed = 110rpm, T = 298K, volume of solution taken: 40 mL)

*Effect of Carbon Dosage and Particle Size*

The study of carbon dosage on removal of Cr (VI) ions was carried out in a batch system using carbon dose of 0.1- 1.00 gram and initial Cr (VI) ions concentration of 70 mg/L at 298K (Fig. 3). The results indicated that the % removal of Cr (VI) ions increased with increase in the adsorbent dose due to increased surface area and the availability of more sorption sites for the metal ions until a saturation limit was reached [20-21]. However, with increase in

carbon dose from 0.1 to 1.00 g, the amount of Cr (VI) ions adsorbed decreased from 14.9 to 2.75 mg/g. The decrease in adsorption capacity could be attributed to the reduction in the effective surface area as a result of aggregation of adsorbent particles in chunks. The active sites of the clustered adsorbent particles are not readily accessible by the metal ions in solution, thereby decreasing the adsorption capacity/adsorption density.

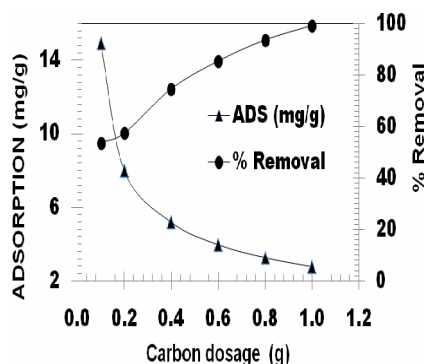


Fig. 3: Effect of Carbon Dosage on Cr (VI) adsorption.

(Cr (VI): 70mg/L, Shaking speed = 110rpm, T = 298K, volume of solution taken: 40 mL)

The effect of variation of particle size of activated carbon from U.S. mesh number +50 (297 micron) to +200 (74 micron) on adsorption of Cr (VI) ions from aqueous solution of initial concentration (70 mg/L) demonstrated that the amount of metal ions adsorbed by the prepared carbon sample increased from 8.0– 21.2 mg/g (and % removal from 28.9-76.2) with the decrease in the carbon particle size from 297-74 micron. The increased adsorption by finely divided particles might be due to larger number of available adsorption sites, increased surface area and the reduction in resistance to the external mass transfer [14, 22].

*Effect of Temperature*

Temperature is one of the most important factors that strongly influence the adsorption of metal adsorbates onto porous adsorbents by increasing or decreasing the interaction between metal ions and adsorbent surface. The study of the effect of temperature change (298 – 328K) on adsorption of Cr (VI) ions from solutions of initial concentrations 30, 70 and 150 mg/L at pH 4 indicated that higher adsorption occurred at higher temperatures. The increase in adsorption with temperature rise suggested the endothermic nature of the adsorption process. The enhanced adsorption capacity might be

due to creation of some new active sites on adsorbent surface, increase in chemical interactions between metal ions and adsorbent particles or due to increase in intra-particle diffusion of metal ions into the pores of the adsorbent at higher temperatures. Several studies have reported similar effects of temperature rise on Cr (VI) ions adsorption [6, 22 and 23].

*Adsorption Isotherms*

An adsorption isotherm correlates the amount of an adsorbate adsorbed ( $q_e$ ) and its equilibrium concentration ( $C_e$ ) in solution. A number of adsorption isotherms can be used to judge the adsorption capacity of various adsorbents and the best fitting of the isotherms to explain the adsorption mechanism. Each isotherm has characteristic constants which values indicate the surface properties and affinity of the adsorbent. To assess the adsorption capacity of the prepared activated carbon samples, Langmuir, Freundlich and Dubinin - Radushkevich isotherm models were applied to the adsorption data.

*Langmuir's Isotherms*

Langmuir's isotherm model is the most widely used isotherm model that gives the maximum adsorption capacity by complete monolayer formation on the homogeneous adsorbent surface without any interaction among adsorbed molecules. It assumes uniform adsorption on the adsorbent surface and once an adsorbate molecule is adsorbed on an active site, no further adsorption at this site and no transmigration of adsorbate molecules in the plane of the surface can occur [24]. The most commonly used linear form of Langmuir isotherm model is

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b_o} + \frac{C_e}{q_{max}}$$

where  $C_e$  is the concentration of metal ions in solution at equilibrium,  $q_e$  is the amount of adsorbate adsorbed onto adsorbent ( $mg.g^{-1}$ ) at equilibrium;  $b$  is the adsorption equilibrium constant ( $mgL^{-1}$ ) that gives the affinity b/w adsorbate and adsorbent and is related to the apparent energy of adsorption and  $q_{max}$  is the maximum monolayer capacity of the adsorbent ( $mg.g^{-1}$ ). Linear plots of  $C_e/q_e$  against  $C_e$  were obtained for adsorption of Cr (VI) ions as shown in Fig. 4 which indicated the applicability of Langmuir isotherm model to the adsorption data. The values of

$q_{max}$  and  $b$  were calculated from the slopes and intercepts respectively of the linear plots of  $C_e/q_e$  against  $C_e$  as shown in Table-2. From Table-2, it can be observed that the values of regression co-efficient  $R^2$  were higher than 0.99 and the calculated values of  $q_{max}$  (28.09 - 37.04  $mg/g$ ) closely agree with the experimental  $q_e$  values of 23.19 - 33.27  $mg/g$ . These facts indicate the best fitness of Langmuir isotherm model to describe the experimental data. The values of  $q_{max}$  and  $b$  increased with increase in temperature which further revealed that the Cr (VI) ions adsorption on the prepared carbon sample was endothermic in nature and favorable at higher temperatures [5, 8, and 25].

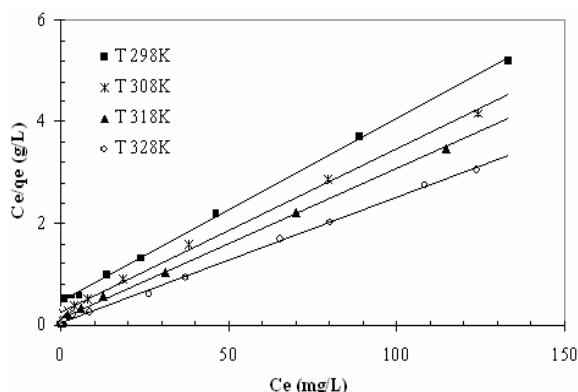


Fig. 4: Langmuir's isotherms for Cr (VI) adsorption by activated carbon.

Langmuir isotherm can also be expressed by a dimensionless constant called equilibrium parameter or separation factor ( $R_L$ ) which is given by Weber and Chackravorti [26] as follow

$$R_L = \frac{1}{1 + b C_i}$$

where  $b$  is the Langmuir constant and  $C_i$  is the initial Cr (VI) ions concentration ( $mg/L$ ),  $R_L$  values indicate the type of isotherm. When  $R_L > 1$ , the adsorption is unfavorable, when  $R_L < 1$ , the adsorption is favorable, when  $R_L = 1$ , the adsorption is linear and when  $R_L = 0$ , the adsorption is irreversible. The  $R_L$  values for adsorption of Cr (VI) ions by the prepared carbon sample are shown in Table-2. The table also reveals that values of  $R_L$  at all temperatures were in between 0 and 1, which indicated the favorable adsorption of Cr (VI) ions onto the carbon sample.

Table-2: Isotherm constants for Cr (VI) adsorption by the prepared activated carbon.

T(K)	Langmuir's constants				Freundlich's constants				D - R constants			
	R <sup>2</sup>	R <sub>L</sub>	b x 10 <sup>2</sup> (L/mg)	q <sub>max</sub> (mg/g)	R <sup>2</sup>	n	1/n (g/L)	K (mg/g)	R <sup>2</sup>	K x 10 <sup>3</sup> (mol <sup>2</sup> kJ <sup>2</sup> )	q <sub>max</sub> x 10 <sup>-7</sup> (mg/g)	E (kJ/mol)
298	0.999	0.15	8.04	28.09	0.972	2.31	0.43	3.77	0.972	-4.3	3.06	10.78
308	0.998	0.09	13.87	31.25	0.976	2.62	0.38	5.49	0.962	-3.7	3.89	11.62
318	0.999	0.05	25.03	33.78	0.984	3.02	0.33	8.09	0.989	-2.8	3.09	13.36
328	0.999	0.03	46.71	37.04	0.991	3.75	0.27	11.3	0.966	-2.2	2.86	15.08

*Freundlich's Isotherms*

The Freundlich's isotherm is the most commonly used adsorption isotherm model which describes the adsorption on heterogeneous surfaces with interactions among adsorbed molecules. It helps to investigate the nature of adsorption and the adsorption capacity of an adsorbent [27]. The linear form of Freundlich isotherm model is

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

where  $K_F$  (mg/g) is Freundlich's constant showing the adsorption capacity of the adsorbent related to the bonding energy and  $n$  is a constant which gives the intensity of adsorption. When  $1/n = 1$ , the adsorption is linear, when  $1/n < 1$ , the adsorption is chemical in nature and when  $1/n > 1$ , the adsorption is physical in nature [26-28]. Freundlich's isotherms (of  $\ln q_e$  against  $\ln C_e$ ) were linear (Figures are not shown) and the values of  $K_F$  and  $n$  were calculated from the intercepts and slopes of the linear plots. It is clear from Table-2 that the values of regression coefficient  $R^2$  were higher than 0.97 for all samples, indicating the applicability of Freundlich isotherm model to the experimental data. The values of  $1/n$  were found less than unity which indicated the chemical nature of adsorption. The increase in  $K_F$  and  $n$  values with temperature rise from 298k to 328k the feasibility of Cr (VI) ions adsorption at higher temperatures [7].

*Dubinini-Radushkevich (D-R) Isotherms*

Dubinini and Radushkevich's isotherm is more general than Langmuir's model. It doesn't account for homogeneous surfaces. It helps to differentiate b/w chemisorption and physisorption in terms of free energy of adsorption [8]. The linear form of D - R isotherm is

$$\ln q_e = \ln q_{max} - K\varepsilon^2$$

where  $K$  is a constant related to the adsorption energy;  $q_{max}$  is the maximum adsorption capacity;  $\varepsilon$  is Polayni potential and can be calculated as follow.

$$\varepsilon = RT \ln \left( \frac{1+q}{C_e} \right)$$

Straight lines were obtained by plotting  $\ln q_e$  against  $\varepsilon^2$  (Figures are not shown). The constants  $K$  ( $\text{mol}^2.\text{kJ}^{-2}$ ) and  $q_{max}$  (mg/g) were calculated from the slopes and the intercepts of the linear plots. The

mean free energy of adsorption ( $E$ ) was calculated from the  $K$  - values as follow.

$$E = \frac{1}{\sqrt{2K}}$$

The values of  $K$ ,  $q_{max}$  and  $R^2$  determined from the linear plots of  $\ln q_e$  against  $\varepsilon^2$  are shown in Table-2. Table-2 shows that the values of mean free energy of Cr (VI) ions adsorption ranged from 10.78 – 15.81  $\text{kJ}.\text{mol}^{-1}$  which indicated that the adsorption process involved an ion-exchange mechanism. The values of mean free energy of adsorption ( $E$ ) for an ion-exchange mechanism range from 8 - 16  $\text{kJ}.\text{mol}^{-1}$ . The values of  $R^2$  for all the samples were higher than 0.96 which revealed that D - R isotherm model can reasonably explain the experimental data [7, 28].

*Thermodynamics of Adsorption*

From the equilibrium data of Cr (VI) ions adsorption at four different temperatures from 298 - 328K, the important thermodynamic parameters such as free energy change  $\Delta G$  ( $\text{kJ}.\text{mol}^{-1}$ ), enthalpy change  $\Delta H$  ( $\text{kJ}.\text{mol}^{-1}$ ) and entropy change  $\Delta S$  ( $\text{J}.\text{mol}^{-1}.\text{K}^{-1}$ ) were evaluated. Free energy change ( $\Delta G^\circ$ ) was calculated from the following relation.

$$\Delta G = \Delta H - T\Delta S$$

$\Delta H$  and  $\Delta S$  were calculated from Vant Hoff's equation, shown below.

$$\ln b = - \Delta H/RT + \Delta S/R$$

where  $b$  is standard thermodynamic constant and its value was calculated from the Langmuir plots of  $C_e$  versus  $C_e/q_e$ . The values of  $\Delta H$  and  $\Delta S$  were calculated from slopes and intercepts of the Vant Hoff's plots of  $\ln b$  versus  $1/T$  as follow.

$$\text{Slope} = - \Delta H/R \quad \text{and} \quad \Delta H = - \text{Slope} \times R$$

$$\text{Intercept} = \Delta S/R \quad \text{and} \quad \Delta S = \text{Intercept} \times R$$

The plot of  $\ln b$  versus  $1/T$  (Vant Hoff's) for Cr (VI) ions adsorption is shown in Fig. 5 and the values of various thermodynamic parameters are shown in Table-3. It can be seen from the table that the values of  $\Delta G$  decreased with temperature rise from 298 to 328K. The negative values of  $\Delta G$  suggested the feasibility and spontaneity of adsorption process. It can also be observed that the values of  $\Delta G$  become more and more negative with temperature rise which revealed that the adsorption was more favorable at higher temperatures. The positive value of  $\Delta H$  indicated the endothermic nature of the process while positive  $\Delta S$  value revealed

greater affinity b/w the activated carbon and Cr (VI) ions and hence favorable adsorption. The positive  $\Delta S$  values also suggested an increased randomness at adsorbent – adsorbate interface which might be due to some structural changes in the active sites of the adsorbent and the Cr (VI) ions during the adsorption process. The adsorbed solvent molecules which were displaced by the metal ions might have gained higher energy and caused more randomness of the system. Similar observations have been reported by several other researchers [7, 19-21].

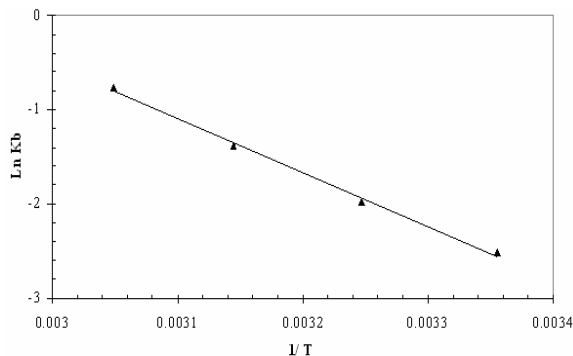


Fig. 5: Vant Hoff's plot for Cr (VI) adsorption by activated carbon.

Table-3: Thermodynamic parameters of Cr (VI) adsorption by the prepared activated carbon.

T (k)	$\Delta G$ (kJ/mol)	$\Delta H$ (kJ/mol)	$\Delta S$ (J/mol.K)
298	-41.215		
308	-42.60		
318	-43.98	47.60	138.47
328	-45.37		

*Kinetics of Adsorption*

Kinetic study of adsorption helps to predict the rate and mechanism of adsorption and to select the most optimum operational conditions for a batch process. Adsorption of metal ions on adsorbents may involve several steps and different mechanisms which depend on various factors including nature of adsorbates and adsorbents. Several kinetic models can be used to explain the mechanism of the adsorption processes [24-26, 29, 30]. The kinetic data obtained for Cr (VI) ions adsorption was analyzed by applying pseudo first-order, pseudo second-order and intra-particle diffusion model. The consistency and conformity between the experimental data and the predicted values of models were expressed by the linear regression correlation coefficients ( $R^2$ ). A

model with  $R^2$  values nearer to 1, indicated that the model provides more successful explanation of the kinetic data. The intra-particle and Elovich diffusion model are not discussed over here due to no close agreement between the calculated values and the experimental data.

*Pseudo-First Order Equation*

The following linear form of Lagergren's differential pseudo first order equation was used

$$\log\left(\frac{qe}{qe - qt}\right) = \frac{k_1}{2.303} t$$

Straight lines were obtained by plotting  $\log(qe - qt)$  versus  $t$  (Figures are not shown). The values of  $k_1$  and  $qe$  were calculated from the intercepts and slopes of the linear plots. The values of rate constant  $k_1$ , equilibrium adsorption capacity  $qe$  and linear regression correlation co-efficient  $R^2$  of pseudo first order kinetic equation are shown in Table-4. The  $R^2$  values for Cr (VI) adsorption were found lower than 0.90 at all temperatures. The calculated  $qe$  values obtained from the linear plots didn't agree with the experimental values which indicated that pseudo first order kinetic equation couldn't explain the adsorption data adequately [7, 30].

*Pseudo-Second Order Equation*

The following linear form of pseudo second order rate equation was used

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

Straight lines were obtained by plotting  $\log(t/q_t)$  versus  $t$  as shown in Fig. 6. The values of  $k_2$  and  $qe$  were calculated from the intercepts and slopes of the linear plots and shown in Table-4. It can be seen from the table that  $R^2$  values for adsorption of Cr (VI) ions on the prepared carbon sample were higher than 0.99. The values of  $qe$  were also found closer to the experimental data which indicated that pseudo second order rate equation is better fitted to describe the adsorption kinetic data. Fitting of the pseudo second order rate equation also suggested that the adsorption of Cr (VI) ions on the prepared carbon sample was of chemical nature [3, 7, 30].

Table-4: Kinetic constants for Cr (VI) adsorption by the prepared activated carbon.

T (K)	Pseudo-1 <sup>st</sup> order model			Pseudo-2 <sup>nd</sup> order model			Intra-particle diffusion model		
	$R^2$	$K_1 \times 10^{-3}$	$q_1$	$R^2$	$K_2 \times 10^{-4}$	$q_2$	$R^2$	$K$	$C$
298	0.894	13.36	8.492	0.998	16.37	27.32	0.698	0.782	4.258
308	0.858	12.21	9.049	0.993	23.09	28.25	0.679	0.873	5.352
318	0.882	12.21	10.70	0.991	19.96	30.12	0.639	0.936	6.791
328	0.864	11.28	11.41	0.996	20.69	34.96	0.671	1.067	7.741

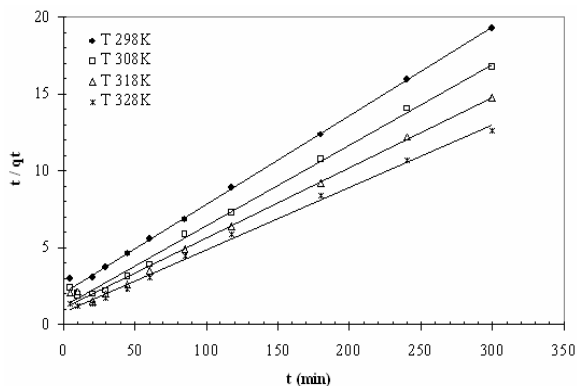


Fig. 6: Pseudo - second order model plots for Cr (VI) adsorption.

#### Intra-Particle Diffusion Model

Intra-particle diffusion model is applied to ascertain intra-particle diffusion as a rate determining step in the adsorption of metal ions from aqueous solution. The intra-particle diffusion may lead to chemical interactions between metal ions and active sites on the adsorbent surface in the form of ion-exchange, complexation reaction and/or chelation. It is usually a slow process and thus may be the rate-determining step of the adsorption process. According to Weber and Morris [31], the intra-particle diffusion model may be expressed as

$$qt = Kxt^{1/2}C$$

where  $qt$  ( $\text{mg}\cdot\text{g}^{-1}$ ) is amount of metal ions adsorbed in time  $t$ ,  $K$  ( $\text{mg}^{-1}\text{g}\text{min}^{-1/2}$ ) is the intra-particle diffusion rate constant and  $C$  ( $\text{mg}\text{g}^{-1}$ ) is related to the thickness of the boundary layer. The values of  $K$  and  $C$  are calculated from the slope and intercept of the plots of  $qt$  against  $t^{1/2}$ . Linear plots of  $qt$  versus  $t^{1/2}$  indicate that adsorption process involves the intra-particle diffusion. Intra-particle diffusion is the controlling step if the straight line passes through the origin. The plots of  $qt$  against  $t^{1/2}$  for adsorption of Cr (VI) ions on the prepared carbon sample were straight lines (Figures are not shown) but not passing through the origin. Moreover, the values of the correlations coefficients  $R^2$  were also lower than 0.90. These results indicated that the intra-particle diffusion was involved but not the only rate controlling step for the adsorption of Cr (VI) ions on the prepared carbon sample [7].

#### Regeneration of Spent Carbon

Desorption of adsorbed metal ions from the activated carbon was carried out by treating with HCl solution. The carbon loaded with metal ions was separated by centrifugation and washed gently with de-ionized water to remove any un-adsorbed metal

ions. The spent carbon was shaken 0.1 M HCl solution for 5 hours and the concentration of desorbed metal ions in filtrate was determined by using atomic absorption spectrophotometer [32]. The adsorption-desorption process was repeated three times and the adsorption capacity of the regenerated carbon was tested which reduced from 95.83% to 88%.

#### Comparison with Other Adsorbents

The adsorption efficiency of the activated carbon sample prepared from the saw dust of *Ziziphus jujube* (Ber) for the removal of Cr (VI) ions from aqueous solutions was compared with other adsorbents reported in the literature [15, 33-37] as shown in Table-5. Although direct comparison of adsorption capacities of different adsorbents is difficult due to different experimental conditions of adsorption like pH, initial concentrations, temperature, adsorbent dosage and shaking speed *etc.*, but still it can be seen from the table that the prepared saw dust activated carbon sample has reasonable capacity for Cr (VI) ions adsorption from aqueous solution at pH 4 which is closer to the pH of natural and wastewaters. Thus the prepared activated carbon can be used successfully as low cost environment - friendly adsorbent for removal of Cr (VI) ions from potable and wastewaters.

Table-5: Comparison of adsorption capacity of the prepared activated carbon with other adsorbents.

Type of adsorbent	Absorption capacity (mg/g)	Optimum pH
Hazelnut-AC	170.0	1.0
Neem leaves	63.0	2.0
Black tea leaves	45.5	2.0
As-received CAC	4.7	6.0
Nitric-oxidized CAC	15.5	4.0
Alligator weed	82.6	1.0
OS-Sulfuric acid AC	71.0	1.5
HSAC	170.0	1.0
Tyres activated carbon	58.5	2.0
Coconut shell carbon	20.0	2.0
HSAC	17.7	2.0
Beech sawdust	16.1	1.0
Sugarcane bagasse	13.4	2.0
Coconut shell carbon	10.9	4.0
Coconut tree sawdust	3.6	3.0
Saw dust AC (Present work)	23.2	4.0

#### Experimental

##### Chemicals

Analytical grade chemicals of high purity were used without any further purification. Phosphoric acid (50%w/w) solution was prepared by dissolving an appropriate amount of  $\text{H}_3\text{PO}_4$  (85%) in triply distilled water. Chromium (VI) stock solution of 1000 mg/L was prepared by dissolving 2.8288g of AR grade  $\text{K}_2\text{Cr}_2\text{O}_7$  in triply distilled water. Working solutions of different concentrations were prepared

from the Cr (VI) stock solution by dilution method. The initial pH of each working solution was adjusted by using dilute solutions of HCl and/or NaOH.

#### *Equipments*

All the solid samples were weighed on Electronic balance (model Ax 120, SHIMADZU JAPAN) and liquid samples were measured with grade B measuring / transferring pipettes, burettes and volumetric flasks. The pH measurements were made with a pH meter (model 744, Metrohm) equipped with a combined glass-saturated calomel electrode calibrated with buffer solutions of pH 4.0, pH 7.0 and pH 10.0. The nitrogen adsorption isotherms were determined with a Quantachrome NOVA 2200e, surface area and pore size analyzer. The impregnated precursor material sample was carbonized in a muffle furnace (model No TF 55030C-1 Thermo electron Corporation, USA), washed in Soxhlet extractor and dried in program controller Nebertherm C-19 (model N 7/4 W – Germany). Agitation was done in a thermostat-cum-shaking assembly model No WS 17-2 Sheldon manufacturing Inc. USA. The residual Cr (VI) ions concentrations were determined using atomic absorption spectrophotometer (Shimadzu model AA670).

#### *Preparation and Characterization of Activated Carbon*

Activated carbon sample was prepared from saw dust of *Ziziphus jujube*. The saw dust collected from saw dust mill was washed with single distilled water to remove dust and other water soluble impurities and then dried at 383K for 24 hours. The sample was mixed in 1:1 (weight ratio) with 50% H<sub>3</sub>PO<sub>4</sub> solution and allowed to soak for 24 hours at room temperature. The impregnated sample was heated in a horizontal tube furnace at 443K for one hour under nitrogen flow at the rate of 100 mL per minute and then at 723K for one hour under the same flow rate of nitrogen. The carbonized sample was then cooled to room temperature in the atmosphere of nitrogen and rinsed with doubly distilled water in Soxhlet extractor at 373K until the pH of the rinsing water become neutral or nearly neutral. The sample was dried at 383K for 24 hours, cooled in desiccator and sieved to desired particle size of 170-400 mesh.

The BET surface area and pore structure characteristics were determined by nitrogen adsorption method at 77K using Quantachrome NOVA 2200e, surface area and pore size analyzer. The micro-pore and total pore volume was determined by BJH method from the amount of

nitrogen adsorbed at P/Po 0.3 - 0.99. The meso-pore volume was calculated by subtracting the micro-pore volume from the total pore volume. The acidic and basic surface functional groups of each sample were determined according to Boehm's method [38-39].

#### *pH Measurement*

The pH of aqueous solutions of the prepared activated carbon samples was measured by mixing 0.1 g of each carbon sample with 40 mL Milli-Q water in 250 mL stoppered conical flasks. The mixture was stirred for 2 hours at 298K and then left to stand for 24 hours. After the equilibrium time of 24 hours, the change in the pH was recorded using pH meter model 744, Metrohm.

#### *Determination of Point of Zero Charge (PZC)*

PZC of each prepared activated carbon sample was determined in a 0.10 M sodium chloride (NaCl) solution at pH 7. In 100mL Erlenmeyer titration flasks, 40 mL of 0.10 M NaCl solution was taken. The pH of the solutions was adjusted between 3.00 and 11.00 by adding 0.10 M HCl / NaOH solutions and recorded as initial pH. Then 0.1g carbon sample was added to each flask and shaken for 24 hours on a shaker bath at 298K. After 24 hours shaking, the final pH was recorded and the difference ( $\Delta$ pH) between final pH and initial pH was noted. The PZC values were calculated from the plots of  $\Delta$ pH versus pH.

#### *Adsorption Studies*

Batch experiments were performed by adding 0.1g of a prepared carbon sample to 40 mL of each Cr (VI) ions solution of desired concentration. The initial pH of the solutions was adjusted by adding 0.10 M HCl / NaOH solution. The solutions were shaken with shaking speed of 110 rpm in a shaker bath for 24 hours at 298K. After shaking, the final pH of each solution was recorded and filtered discarding the first 5 mL fraction of each filtrate. The filtrates were analyzed for residual Cr (VI) ions concentrations by using atomic absorption spectrophotometer.

The effect of pH on adsorption of Cr (VI) ions was studied in the pH range of 2 – 7 using three different initial concentrations of 30, 70 and 150mg/L at 298K. The effect of contact time and initial concentration was studied at pH 4 and 298K. Kinetic study was performed using 70 mg/L initial concentration of Cr (VI) ions solution at pH 4 and 298K – 323K. Each solution was agitated for pre-



decided time intervals, filtered and the filtrates were analyzed for residual Cr (VI) ions concentrations. Temperature study was performed at four different temperatures from 298K – 323K with solutions of 30, 70 and 150 mg/L at pH 4. The amount of Cr (VI) ions adsorbed ( $q_e$ ) onto the prepared carbon sample after each batch experiment was calculated by the equation

$$q_e = \frac{(C_i - C_e)V}{W \times 1000}$$

where  $C_i$  and  $C_e$  are the initial and equilibrium concentrations (mg/L) of metal ions in solution, V is the volume (L) and W is the amount of adsorbent in grams.

### Conclusion

1. The acid activated saw dust carbon of *Ziziphus jujube* was found micro-porous in nature with larger BET surface area and lower BJH surface area.
2. Enhanced adsorption of Cr (VI) ions occurred at lower solution pH and higher initial concentration, carbon dosage and temperature.
3. Maximum adsorption of Cr (VI) by the prepared carbon was observed in the pH range of 2 – 4.
4. Adsorption rate was very rapid in the early 60 minutes which then become slower and almost constant after equilibrium time of 300 minutes.
5. Thermodynamic study revealed the adsorption of Cr (VI) was feasible, spontaneous and endothermic in nature.
6. Langmuir's isotherm model and pseudo - second order rate equation were found better fitted to the adsorption data.
7. The adsorption-desorption study revealed that the spent carbon could be regenerated and re-used for adsorption of Cr (VI) ions successfully.
8. As compared to other adsorbents reported in the literature and particularly considering the optimum pH 4 which is closer to pH of natural and wastewaters, it is worthwhile to say that the prepared saw dust activated carbon could be a promising low cost and environment friendly adsorbent for the removal of toxic Cr (VI) ions from aqueous solutions.

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