Chromium(VI) adsorption by sawdust carbon: Kinetics and equilibrium

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The ability of sawdust carbon to remove chromium from aqueous solution by adsorption was investigated according to equilibrium and kinetics. The extent of removal of Cr(VI) is dependent on concentration, pH and temperature of the solution. With an initial concentration of 100 mg/L and at 60°C and pH 2.5, the removal was found to be 49.8 mg/g. The intra-particle diffusion of Cr(VI) through pores in the adsorbent was shown to be the main rate limiting step. The higher uptake at pH 2.5 was attributed to chemical reduction of Cr(VI) to Cr(III) coupled with physico-chemical adsorption of Cr(VI) species. The Langmuir and Freundlich adsorption isotherms were used to represent the experimental data. The Langmuir and Freundlich constants were calculated at different temperatures and the adsorption capacity for Cr(VI) increases with temperature. The method was applied on synthetic wastewaters. Treatment of the exhausted carbon with 0.1 M NaOH removed only 87.2% of the adsorbed chromium, suggesting that the binding to the carbon involved strong chemisorption forces.

Chromium, particularly in its hexavalent form, is a well known highly toxic metal, considered as priority pollutant¹. The main industrial sources of chromium pollution are leather tanning, electroplating, paint and pigment, textile, dyeing and canning industries¹. Principle techniques for recovering or removing chromium from wastewater are-chemical reduction and precipitation, ion exchange and $adsorption^2$. First method is reliable, but requires large settling tanks for precipitation of voluminous chromium hydroxides and subsequent sludge treatment. Ion exchange has the advantage of recovery of Cr(VI), but it is more expensive and sophisticated. Recently removal of Cr(VI) by adsorption using activated carbon has been developed into a promising alternative, even for smaller plating plants, the method appears to be economically feasible². Activated carbons prepared from low cost materials such as coconut shell², coconut jute³, tea leaves⁴ and rice husk⁵ have been used for the removal of Cr(VI) from aqueous solutions. Sawdust from timber industry is considered as waste material and widely available. Iron impregnated sawdust has been used as an adsorbent for phenolic compounds by Singh and Mishra⁶. Cullen and Siviour⁷ studied the adsorption of metals on sawdust. Recently, phosphate treated sawdust was used for the removal of chromium from wastewater⁸. Some preliminary investigations on the removal of heavy metal ion with polymer grafted sawdust have been reported by Raji and Anirudhan^{9,10}. The present investigation reveals the adsorption capacity of sawdust based carbon for the removal of Cr(VI) under varied aqueous environmental conditions, by batch adsorption technique. The desorption studies have also been carried out.

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Experimental Procedure

The sawdust of rubber wood (Hevea braziliansis) procured locally was treated with hot distilled water and dried at 100°C. Sawdust carbon (SDC) was prepared by reacting 10 g of sawdust with 10 mL of concentrated sulphuric acid and heating to 150°C for 12 h. The carbonized material was washed with distilled water to remove excess of acid and dried at 100°C. Before utilization of the adsorbent, SDC is ground and sieved to -80+230 mesh size.

FTIR spectra of SDC was recorded on a Bruker IFS 66V spectrophotometer between 400-4000 cm⁻¹. The IR spectra of SDC shows weak peaks in the region 1800-1600 cm⁻¹. The band at 1730 cm⁻¹

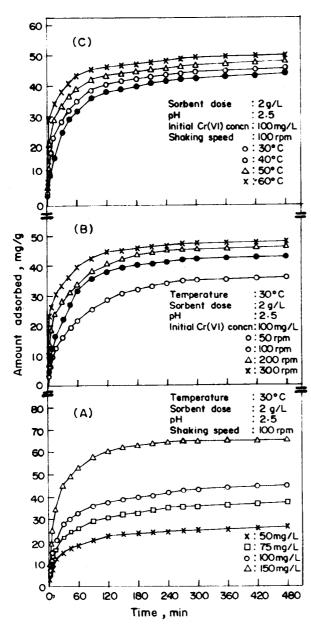


Fig. 1—Effect of agitation time on the adsorption of Cr(VI) on SDC. (A) At different initial concentration, (B) At different shaking speed, (C) At different temperatures.

corresponds to a normal carbonyl group¹¹ while the one at 1665 cm⁻¹ may be attributed to conjugated hydrogen bonded carbonyl groups as suggested by Hallum and Drushell¹². The adsorbent was analysed for a number of physical and surface properties by standard methods^{9,13}. The characteristics of the sorbent are—apparent density—1.31 g/mL, surface area—226 m²/g, porosity—0.68 mL/g moisture

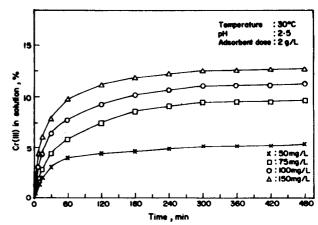


Fig. 2—Effect of agitation time on the reduction of Cr(VI) on SDC at different initial concentration.

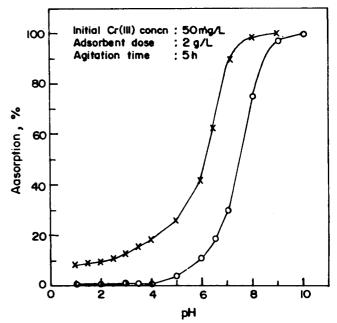


Fig. 3—The removal of Cr(III) at a range of pH values. Removal without SDC, O—O removal in the presence of SDC, x—x.

content -1.8%, cation exchange capacity 1.41 meq/g, and p^{H}_{2pc} --5.8.

Batch experiments were carried out by shaking 50 mL of Cr(VI) solution of desired concentration and pH at different temperatures with 100 mg of SDC in an electric shaker. A shaking speed of 100

rpm was used unless otherwise stated. Aliquot of supernatant was withdrawn at different time intervals and the amount of Cr(VI) in the solution was estimated by spectrophotometric method¹⁴. Cr(III) was calculated as the difference between total chromium and Cr(VI).

Desorption study was carried out by taking 100 mg of Cr(VI) loaded SDC and 50 mL' aqueous solution of NaOH and agitating for 6 h at 100 rpm. Further procedure was same as followed for adsorption and the amount of desorbed chromium was estimated.

Results and Discussion

Effect of agitation time and initial concentration-The effect of agitation time on Cr(VI) removal was investigated using different initial concentrations at pH 2.5. Fig. 1 shows that removal of Cr(VI) reached equilibrium in approx 210, 240, 270 and 300 min for initial Cr(VI) concentration of 50, 75, 100 and 150 mg/L respectively. This indicates that the equilibrium time is dependent on the initial concentration probably because the adsorption sites adsorbed the available chromium more quickly at low solute concentrations. However, for higher concentrations, intra-particle diffusion or creation of new sites were predominant adsorption mechanisms¹⁵. The removal curves are single, smooth and continuous indicating the possibility of the formation of monolayer of Cr(VI) ions on the outer surface of the SDC and pore diffusion into the inner surface of the adsorbent particle through the film due to continuous agitation maintained during the experiments 16,17

Variations of Cr(VI) removal with time at different shaking speed and temperature are shown in Fig. 1. The Cr(VI) removal increased with time and attained almost an equilibrium condition at about 270 min for all the shaking speeds investigated. It is also observed that the rate of increase of Cr(VI) removal is more up to 180 min, which has significantly decreased beyond 180 min till equilibrium stage is attained. The removal of Cr(VI) increased with increase in shaking speed. An enhanced removal at higher shaking speed is probably due to the decrease in boundary layer thickness surrounding the adsorbent particle¹⁸. A similar observation was also made by Mckay *et al.*¹⁸. The removal of Cr(VI) by sorption on SDC increases from 43.29 mg/g (86.58%) to 48.50 mg/g (97.0%) by increasing temperature of solution from 30 to 60°C indicating process to be endothermic. In the present work, it was found that higher temperature aids the adsorption process. This may be due to increase in diffusivity with temperature which can eventually transport more Cr(VI) ions to the carbon surface or may be due to the increased surface activity which increases adsorption or may be due to both the effects¹⁹.

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Adsorption kinetics—The amount of reduction of Cr(VI) into Cr(III) when equilibrated over the concentration range 50-150 mg/L, is plotted in Fig. 2. The data indicate that the conversion of Cr(VI) to Cr(III) occurs up to the extent of 12.5% over the concentration range 50-150 mg/L. In order to understand the adsorption mechanism, additional experiments on the adsorption of Cr(III) onto SDC were also performed and results are shown in Fig. 3. It was found that some Cr(III) was also adsorbed onto SDC in acidic solutions. In acidic medium, the reduction of Cr(VI) proceeds according to

$$\operatorname{Cr}_2\operatorname{O}_7^2 + 14\operatorname{H}^+ + 6e^- \leftrightarrow 2\operatorname{Cr}^{3+} + 7\operatorname{H}_2\operatorname{O}$$

(1)

r

The amount adsorbed versus time plot (Fig. 1) shows that the adsorbent was capable of removing Cr(VI) over the entire duration of study. It has been observed that though in the beginning the uptake was rapid it subsequently changed to a much slower rate. First stage adsorption is the fast reaction leading to 'almost equilibrium conditions' within 30 min after which a near, linear rate of decrease is quite apparently revealed and leading to 'equilibrium' within 300 min²⁰. Also the two stages of adsorption observed in the present study are in agreement with the conclusions of earlier workers⁴, that the sorption of chromium by carbon follows a two stage kinetics. Results for the second adsorption step fitted the equation of a second order reversible process¹⁵. Assuming reversible adsorption involving a chromate ion (Cr) in solution and the adsorbed species Cr' and Cr", the process may be represented according to Fox et al.¹⁵

$$2Cr \Leftrightarrow Cr' + Cr'' \qquad \dots (2)$$

where the conditional rate constant, k_1 may be calculated using the equation

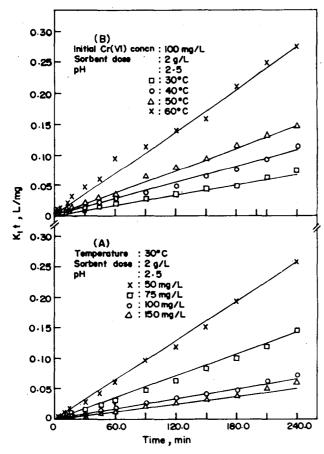


Fig. 4—Plots of k_{1t} versus t for the adsorption of Cr[VI] on SDC. (A) At different concentrations, (B) At different temperatures.

$$k_1 t = \frac{C_o - C_\alpha}{2C_o C_\alpha} \ln \left[\frac{C_o C_\alpha - 2C_t C_\alpha + C_t C_o}{C_o (C_t C_\alpha)} \right] \qquad \dots (3)$$

where C_0 , C_t and C_{α} refer to concentration at time o, t and α respectively.

Kinetic plots of the data, presented in Fig. 4, were found to be linear with correlation coefficient (r) of more than 0.968, indicating a strong relationship between the parameters. The k_1 values from the slopes of the plots are 10.740×10^{-4} , 5.925×10^{-4} , 2.820×10^{-4} and 2.063×10^{-4} L/mg/min for the initial Cr(VI) concentrations of 50, 75, 100 and 150 mg/L respectively. The k_1 values increased with decreasing initial concentration. The linearized k_1 and C_0 values on a double logarithmic plot showed a correlation coefficient (r) of 0.98, the relationship between k_1 and C_0 being of the type

$$k_1 = -0.318 C_0^{-1.569.}$$
 .. (4)

Table 1—Intra-particle diffusion rate constant $[k_p]$ and diffusion coefficient [D] for the adsorption of Cr(VI) on SDC

Initial concn	k _p	D
mg/L	mg/g/min ^{1/2}	m ² /S
50	0.167	5.485×10 ⁻¹⁴
75	0.204	6.400×10 ⁻¹⁴
100	0.220	7.432×10 ⁻¹⁴
150	0.333	9.601×10 ⁻¹⁴
Shaking speed, r.p.m.		
50	0.190	3.200×10 ⁻¹⁴
100	0.220	7.432×10 ⁻¹⁴
200	0.416	9.630×10 ⁻¹⁴
300	0.476	19.20×10 ⁻¹⁴
Temperature, °C		
30	0.220	7.432×10 ⁻¹⁴
40	0.267	9.621×10 ⁻¹⁴
50	0.406	12.80×10 ⁻¹⁴
60	0.500	28.80×10 ⁻¹⁴

The quality of this correlation supports the assumptions concerning the kinetics, particularly the assumption of a chemical rate limiting step. The k_1 calculated from the slopes of the plots at 30, 40, 50 and 60°C are 2.820×10^{-4} , 4.546×10^{-4} , 6.094×10^{-4} and 11.56×10^{-4} L/mg/min respectively (Fig. 4). This increase in k_1 values with increase of temperature shows that sorption is greater at higher temperatures and suggests that active surface centers available for sorption has increased with temperature.

Intraparticle diffusion—In any rapidly stirred process the existence of intraparticle diffusion cannot be overruled, besides the adsorption at the outer surface of the adsorbent which are often the limiting steps. The plot of q, amount of Cr(VI) adsorbed per unit weight of adsorbent versus time^{1/2}, has been commonly used to describe whether the adsorption process is controlled by intraparticle diffusion. The double nature (curved and linear) plots were obtained for the adsorption process at different concentration, shaking speed and temperature indicating

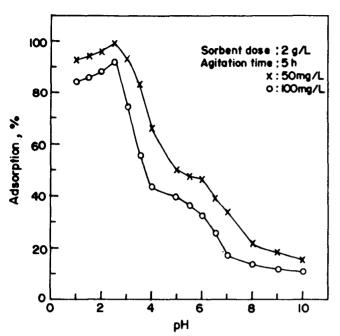


Fig. 5-Effect of pH on the adsorption of Cr(VI) on SDC

the existence of intraparticle diffusion in the adsorption process¹⁸. The initial curved portion representing the film diffusion and subsequent linear portion representing the film diffusion and subsequent linear portion representing intraparticle diffusion. The values of intraparticle diffusion rate constant, k_p for different concentration, shaking speed and temperature were calculated from the slopes of the linear portion of the respective plots and are given in Table 1. k_p was higher at higher concentration and higher shaking speed. The values also suggest that sorption is faster at higher temperature.

The pore diffusion coefficients $D(m^2/s)$ for adsorption of Cr(VI) into SDC at various concentrations, shaking speed and temperature were calculated by the method of Vermeulen²¹ as applied by Bhattacharya and Venkobachar²² and Streat *et al.*²³.

$$D = \frac{0.030r_0^2}{t_{1/2}} \qquad \dots (5)$$

where r_0 is the particle size radius and $t_{1/2}$, is time for half adsorption. The calculated values of D for Cr(VI) adsorption into carbon ($r_0=0.096$ mm) are given in Table 1. According to earlier workers^{23,24} for pore diffusion to be rate limiting, the pore

for the adsorpt	-		
Temperature, °C	Langmuir co	Correlation coefficient	
	Q°, mg/g	b, L/mg	(r)
30	130.5	0.0715	0.999
40	138.3	0.0937	0.998
50	150.2	0.1224	0.996
60	155.2	0.1460	0.995

-I anomula constants and correlation coefficients (r)

diffusion coefficients should be in the range of 10^{-12} - 10^{-14} m²/s. As per this, the rate limiting step appears to be pore diffusion for Cr(VI)-SDC system.

Increasing the initial Cr(VI) concentration and shaking speed results in an increase in the *D* values. Increasing the metal concentration in the solution seems to reduce the diffusion of metal ions in the boundary layer and to enhance the diffusion in the solid²⁵. Diffusion of metal ions into SDC is controlled by the degree of agitation. This process would be influenced by the concentration gradient between those two points and the thickness of the diffusion layer which is a function of the agitation process²⁶. The increase in *D* values with temperature may be due to enhanced rate of intraparticle diffusion of sorbate, as diffusion is an endothermic process.

Influence of pH—The effect of pH on Cr(VI) removal, for two different initial Cr(VI) concentrations is presented in Fig. 5. It may be seen that the adsorption of Cr(VI) ions is most appreciable in the pH range from 1.0 to 3.0. For highly acidic pH, up to 2.5, the amount of Cr(VI) removal increases with the increase of pH up to a maximum then decreasing sharply and continuously for pH values higher than 2.5. The same trend has previously been found in literature^{4,5,27}. It has been justified²⁷ by taking into account the affinities of the carbon for different species of Cr(VI), coexisting at acidic $pH(Cr_2O_7^{2-}, HCrO_4^{-}, Cr_3O_{10}^{2-}, Cr_4O_{13}^{2-})$. Cr(VI) removal by SDC is governed by-chemical reduction (i.e., Cr(VI) to Cr(III)) and physico-chemical adsorption of mainly Cr(VI) species. At pH < 2.5, the retention of Cr(VI) was found to be affected by its reduction to Cr(III), the lower the pH the greater the facility to be reduced to Cr(III). It is evident from the Fig. 2 that at the low pH conditions (< 2.5) the adsorption of Cr(III) was poor (< 9.0%). The low

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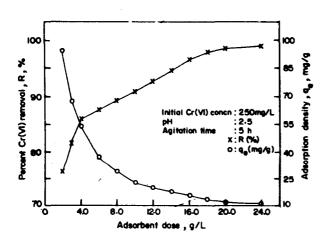


Fig. 6-Effect of adsorbent dose on Cr(VI) removal.

adsorption of Cr(III) at low pH range may be due to its larger coordination sphere with water²⁷. Eventhough, the predominant species at pH < 2.5 is $HCrO_4^{-}$. The carbon can reduce, Cr(VI) to Cr(III) and, since the adsorption of Cr(III) onto carbon decreases with the decrease of pH (Fig. 2), the decrease in Cr(VI) amount removed by carbon when pH is decreased from 2.5 to 1.0 can be explained. Views of similar kind have been put forth by the earlier workers²⁷ who had studied the adsorption characteristics of Cr(VI) with activated carbons.

The surface charge on SDC is zero at about 5.8 (pH_{zpc}) . At $pH < pH_{zpc}$, the SDC surface is slightly positively charged, consequently, coulombic attraction can readily take place in conjunction with specific chemical adsorption due to chemical interaction between HCrO₄ ⁻ and surface oxides of the carbon 2,5 (C_xO/ and C_xO₂). Chemical adsorption involves exchange with hydroxyl ions².

$$C_xO+H_2O+HCrO_4^- \leftrightarrow C_xOHO_3Cr^+ + 2OH^-$$
... (6)

$$C_xO_2 + H_2O + HCrO_4 \xrightarrow{-} \leftrightarrow C_xO_2 HO_3Cr^+ + 2OH^-$$

... (7)

The above reactions lead to an overall pH increase of the solution. Thus, for an initial pH of 2.5, 3.0, 3.5 and 4.5, the final pH for an initial concentration of 50 mg/L were 3.1, 3.7, 4.0 and 4.8 respectively, the corresponding final pH values for an initial concentration of 100 mg/L were found to be 3.5, 3.7, 4.4 and 4.8. The decrease in the Cr(VI) amount removed in the pH region above 2.5 may be ascribed to the increasing concentration of CrO_4^2 which is retained with great difficulty²⁸. When $pH > pH_{zpc}$, the surface is negative and predominant CrO_4^2 species must compete with coulombic repulsion, consequently, adsorption capacity of Cr(VI) is suppressed.

Influence of adsorbent dose-Fig. 6 shows the influence of adsorbent concentration on the amount of Cr(VI) adsorbed by SDC. It is apparent that by increasing the adsorbent dose from 2.0 to 24.0 g/L the removal efficiency increases but adsorption density decreases. Observations of the similar kind have also been reported by other workers³ who studied the adsorption of Cr(VI) on coconut jute carbon. The decrease in adsorption density may be attributed to the fact that the some of the adsorption sites remain unsaturated during the adsorption process, whereas the number of available adsorption sites increases by increasing the adsorbent dose and that results in the increase of removal efficiency. Another reason may be due to the aggregation/agglomeration of adsorbent particles at higher concentration. Such aggregation would lead to a decrease in the total surface area of carbon particles available to Cr(VI) adsorption and an increase in diffusional path length²⁹. The particle interaction brought about by high sorbent concentration may also desorb some of the sorbate which is only loosely and reversibly bound to the carbon surface. The data can also be used to derive a mathematical relationship to relate the Cr(VI) removal to the carbon dose (using adsorbent dose $m_s = 2.0$ to 24.0 g/L). This relationship, for which the correlation coefficient (r) was 0.99, is

$$R = \frac{m_s}{9.27 \times 10^{-3} + 9.78 \times 10^{-3} m_s} \qquad \dots (8)$$

This equation can be used to predict the percentage Cr(VI) removal for any carbon dose within the test limits at pH 2.5 and initial Cr(VI) concentration, C_0 of 250.0 mg/L.

Adsorption isotherm—To determine the adsorption capacity of the SDC, a study of sorption isotherm was attempted by using two models Langmuir and Freundlich isotherms. The Langmuir isotherm can be represented by the following equation.

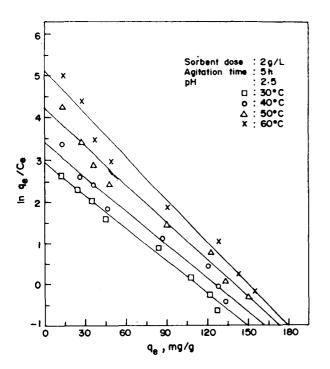


Fig. 7—Plots of $\ln [q_e/C_e]$ versus q_e at different temperatures for the adsorption of Cr(VI) on SDC.

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \qquad \dots (9)$$

where q_e is the amount of Cr(VI) adsorbed per unit mass of sorbent at equilibrium and C_e is the equilibrium liquid phase concentration of Cr(VI). Q^{o} and b are Langmuir constants indicating sorption capacity and energy of adsorption respectively. The plots of C_e/q_e versus C_e at different temperature were found to be linear indicating the applicability of the Langmuir model. The statistical significance of the correlation coefficient (r) for C_e/q_e versus C_e was the criteria by which the fitting of the data to Langmuir isotherm was tested. It demonstrates monolayer coverage of adsorbate at the outer surface of the sorbent. The parameters Q° and b have been calculated and the results are presented in Table 2, showing high correlation coefficient. The Langmuir constants Q^{0} and b increased with temperature, suggesting that adsorption capacity and intensity of adsorption are enhanced at higher temperature.

The Freundlich model was also used to explain the observed phenomena. The equilibrium data were analysed using the linearized equation.

$$\log q_{\rm e} = \log K_{\rm F} + 1/n \log C_{\rm e} \qquad \dots (10)$$

Table 3—Freundlich constants and correlation coefficients (r)and thermodynamic parameters for the adsorption of Cr(VI) on SDC

Tem- pera- ture, °C	Freundlich constants			Thermodynamical parameters	
	Kp	1/n	r	Ko	∆G ^o , kJ/mol
30	16.27	0.409	0.979	18.71	-7.378
40	20.56	0.382	0.984	30.63	-8.905
50	26.61	0.353	0.991	65.49	-11.230
60	34.75	0.313	0.986	171.91	-14.249

Ions/pH	composition of synthetic wastewater Concentration, mg/L		
	Sample I	Sample II	
Cr ⁶⁺	50	75	
Cu ²⁺	20	20	
Ni ²⁺	20	20	
Zn ²⁺	56	56	
Cl⁻	60	60	
SO4 2-	30	30	
pН	5.8	5.4	

where $K_{\rm F}$ and 1/n are Freundlich constants. The plots of log $q_{\rm e}$ versus log $C_{\rm e}$ at different temperatures were found to be linear. The *r* values relating to log $q_{\rm e}$ versus log $C_{\rm e}$ were highly significant in all cases. The $K_{\rm F}$ parameter of Eq. (10) which is a measure of sorption capacity increased with increase of temperature (Table 3). Since the values of 1/n (adsorption intensity) are less than 1, it indicates a favourable adsorption³⁰.

Thermodynamic parameters were calculated from the variation of the thermodynamic equilibrium constant (K_o) with change in temperature and are given in Table 3. K_o for the sorption process was determined by the method of Bigger and Chuang³¹ as applied by Singh *et al.*³² by plotting $\ln q_e/C_e$ versus q_e and extrapolating to zero q_e (Fig. 7). The positive value of ΔH^o (61.66 kJ/mol) support the endothermic nature of the process. Adsorption is found to be more favourable as the free energy of adsorption increases. The negative values of ΔG^o

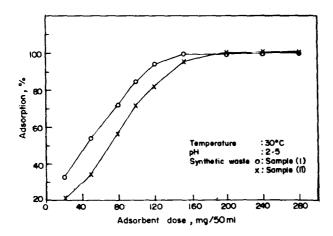


Fig. 8—Effect of adsorbent dose on the adsorption of Cr(VI) from synthetic wastewater.

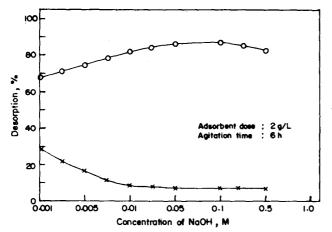


Fig. 9—The desorption of chromium by sodium hydroxide, Cr(VI), O—O; Cr(III), x—x.

indicate the process to be feasible and spontaneous. The positive value of ΔS^{o} (226.03 J/mol/K) suggests the increased randomness at the solid- solution interface during the sorption⁹.

Adsorption of Cr(VI) from synthetic wastewater—The utility of the adsorbent material has been demonstrated by treating synthetic wastewater containing Cr(VI) ions. The composition of synthetic wastewater is given in Table 4. Cations may not interfere at pH 2.5 because the surface charge of SDC is positive. The removal of Cr(VI) from wastewater was 100% at pH 2.5 when 50 mL of the waste was treated with 150 mg of adsorbent, for sample I and 200 mg of adsorbent for sample II (Fig. 8).

Desorption of chromium—Attempts have been made to recover the adsorbed metal as well as regenerate the adsorbent. An extended agitation (for 6 h) of chromium-laden SDC with sodium hydroxide at 30°C was used to elute chromium into solution. The percentage desorption increased with increase in concentration of NaOH and attained a maximum of 87.2% at 0.1 M NaOH (Fig. 9). Under alkaline conditions, the higher desorption may be possibly due to the abundance of OH⁻ causing increased hindrance to diffusion of Cr(VI) jons³³. It was found that some Cr(III) was also eluted by the NaOH (Fig. 9). It appears that chemical reduction of Cr(VI) to Cr(III) occurs at the carbon surface. Experiments on the adsorption of Cr(III) onto SDC also confirm that small quantities of Cr(III) ions are adsorbable onto SDC in acidic solution.

Conclusion

Sawdust carbon is a suitable adsorbent for the removal of Cr(VI) from wastewater. Sorption of Cr(VI) is pH dependent and the best results are obtained in the pH range 1.0-3.0. Regressional analysis showed that experimental data fitted closely the Langmuir and Freundlich isotherms. 100% removal of Cr(VI) from synthetic wastewater containing 50-75 mg/L could be achieved at pH 2.5. The adsorbed chromium can be recovered (87.2%) using 0.1 M NaOH. Mathematical expressions can be derived to describe the adsorption of chromium by SDC and its kinetics. The kinetic data would be useful for the fabrication and designing of wastewater treatment plant.

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