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Removal of Chromium(VI) from Aqueous Solutions Using Activated Carbon Prepared From Flame Tree Seed Coat

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A new low cost activated carbon prepared from flame tree seed coat (FTSC) by acid process followed by thermal activation was used as an adsorbent in the present investigation for the removal of chromium(VI) from its aqueous solution. The efficiency of the activated carbon in the removal of chromium(VI) was studied under various experimental conditions such as dosage of adsorbent, pH and contact time. More than 85 % removal was achieved under optimal conditions. The adsorption obeys Freundlich adsorption isotherm.

Key Words: Chromium(VI), Activated carbon, Flame tree seed coat, Removal.

INTRODUCTION

In the last three decades, national and international bodies responsible for public health have become increasingly anxious about the inorganic constituents and their possible effects on health. Chromium is one among the most common water pollutant[1]. The effluent from the industries like tanneries and chromium plating industries contain chromium. The toxicity of hexavalent chromium from the discharge of various industrial wastes is well documented[2-4]. Chromium is reported to be toxic to cat fish at higher concentration[5]. It also causes cancer in the human beings. A variety of methods have been developed for the removal of toxic and inorganic constituents like heavy metals from water and wastewater. The method that find wide spread use are precipitation, ion exchange, reverse osmosis, activated sludge process and adsorption. Among these process technologies available for the removal of chromium from wastewater, adsorption using activated carbon has been found to be more efficient process. Srivatsava *et al.*[6] have studied adsorption of heavy metals on carbonaceous materials developed from waste slurry of fertilizer plants. Gupta *et al.*[7] examined a locally available fly ash for the removal of chrome dye and reported removal of 99 %. Srinivasan *et al.*[8] examined the carbon derived from rice husk for the removal of Cr(VI) from plating waste.

From the foregoing account it is clear that adsorption using activated carbon is an efficient process to treat wastewater as it renders the water free from both organic and inorganic constituent. However the commercial activated has being relatively

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expensive finds only limited use. Present aim is to make this process an economically viable one using the flame tree seed coat carbon (FTSCC). The investigation reported here deals with the comparative study of the activated carbon derived from flame tree seed coat (*Delonix regia*) with commercially available carbon for the removal of chromium(VI) from aqueous solutions.

EXPERIMENTAL

All chemicals were used of analytical grade. Flame seed coat was used for the preparation of activated carbon. A rotary mechanical shaker (model Neo Lab) was used to carry out the batch studies. Digital pH meter Systronics (Systronics-335), Spectrophotometer (Systronics-106) were used for measuring pH and colorimetric studies.

Preparation of FTSCC carbon: Flame tree seed coat activated carbon (FTSCC) was prepared by mixing 50 g of flame tree seed coat with concentrated sulphuric acid (sp.gr. 1.84) in 1:1.5 weight ratio and heating to 120-150 °C for 12 h. The carbonized material was washed with water followed by 2 % solution of sodium bicarbonate until the effervescence ceases. The char was then separated and dried at 105-120 °C and the dried char was thermally activated at 850 °C for 0.5 h. The material was ground in an agate mortar and the particles having the average diameter of 0.5 mm (20-50 mesh ASTM) was used throughout the study. Various parameters such as bulk density, moisture content, ash content, fixed carbon content, matter soluble in acid, pH, decolourizing power and surface area were determined as per ISI procedure[9] to characterize the activated carbon (Table-1). The characterization studies of FTSCC prepared by acid process followed by thermal activation has revealed that the activated carbon obtained by this process exhibits considerable hardness and bulk density and decolourizing power. This means that the carbon is suitable for wide application in the treatment of wastewater. Therefore using this carbon, batch study experiments were conducted. Commercial granular activated carbon supplied by central drug house, New Delhi was also subjected to similar test for comparative purpose.

TABLE-1
CARBON CHARACTERISTICS

Control tests	FTSCC Acid	CAC
Bulk density (g/cc)	0.3581	0.68
Moisture (%)	6.65	12.57
Ash (%)	4.353	2.91
Fixed Carbon (%)	94.5	97.09
Matter soluble in water (%)	1.84	1.55
Matter soluble in acid (%)	8.46	4.58
pH	5.4	9.2
Decolourising power (mg/g) (methylene blue)	89.91	73.5
Surface area (m^2/g) (N_2 gas B.E.T method)	464	296

CAC = Commercial activated carbon.

Batch experiments: Colorimetric method using diphenyl carbazide reagent was adopted for the determination of chromium. 100 mL of the chromium solution (10 mg/L) was taken in 250 mL reagent bottles and varying amounts of carbon were added to optimize the carbon dosage. The solutions were equilibrated for 24 h at 27 °C in a mechanical shaker. After the equilibration period, the carbons were filtered and the chromium concentration was estimated.

Carbon dosage was fixed at 0.8 g/L and the chromium concentration was varied over the range of 10-50 mg/L for kinetic studies. Suitable aliquots were withdrawn at regular interval of time for estimating chromium concentration. The rate constants were calculated by employing the conventional rate equation[10].

RESULTS AND DISCUSSION

The effect of variation of experimental parameters such as pH of the solution, dosage of adsorbent, duration of the equilibration of the aqueous solution of chromium with the activated carbon on the uptake of chromium on activated carbon was examined.

The optimum pH for any adsorption process is usually determined by laboratory batch studies. The adsorption studies were conducted over a pH range 1-11. The pH of the aqueous solution of chromium has been found to affect its uptake on activated carbon and in general the uptake decreases at higher pH. Maximum removal of chromium (98 %) occurs at pH range 1-2.5 (Fig. 1). Hence the solution pH of 2.5 was maintained in the studies. The commercial activated carbon showed a maximum removal of 91 % at pH 1 and it could remove only about 60 % of Cr(VI) at pH 2.5.

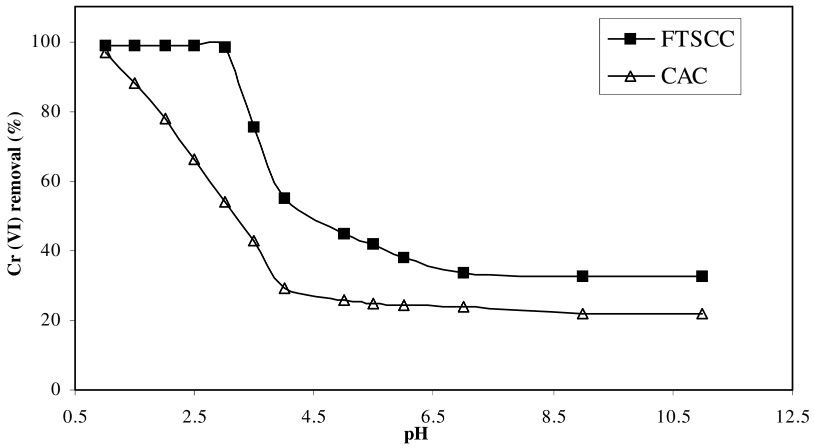

Fig. 1. Effect of pH on the removal of Cr(VI) by FTSCC and CAC

Fig. 2 shows the amount of chromium recovered as a function of carbon dose. The percentage removal of chromium increases with increasing carbon dosage. This is mainly due to the substantial increase in the surface area of the adsorbent. The optimum dosage of FTSCC for maximum removal of chromium has been found to be 0.8 g/L. The low optimum dose of FTSCC may be attributed to the greater adsorptive capacity whereas the optimum dosage of CAC for the maximum removal of chromium was found to be 1.2 g/L. The CAC was able to remove only 80 % of Cr(VI) with 0.8 g/L of carbon while the FTSCC was able to remove more than 96 % of Cr(VI). Beyond the optimum dosage further addition of carbon dosage does not show any significant removal efficiency. This is due to the overlapping of active site at higher concentration which reduces the effective surface area[11].

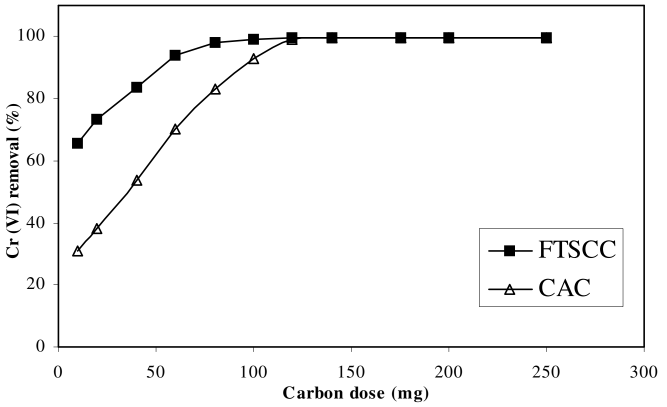

Fig. 2. Effect of carbon dose on the removal of Cr(VI) by FTSCC and CAC

Fig. 3 shows the effect of contact time on the percentage removal of chromium. The uptake of chromium by activated carbon is rapid initially, decreases gradually and remains constant after 8 h. The optimum period of contact time for adsorption is found to be 6 h.

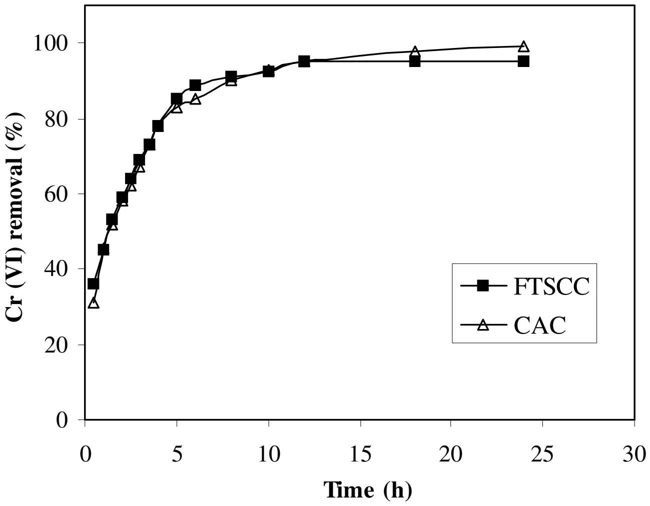

Fig. 3. Effect of contact time on the removal of Cr(VI) by FTSCC and CAC

The experimental results (Table-2) obtained for the adsorption of chromium on FTSCC and CAC at room temperature (27 ± 1 °C) at optimum carbon dosage and time were found to obey Freundlich adsorption isotherm.

$$(x/m) = KC_e^{1/n}$$

where x = amount of chromium removal (mg), m = amount of activated carbon (g), C_e = equilibrium concentration, K and n are Freundlich constant, respectively.

TABLE-2
DATA OF FREUNDLICH ADSORPTION ISOTHERM FOR VARIOUS INITIAL CONCENTRATION OF Cr(VI) WITH FTSCC AND CAC

Adsorbent (mg)	Initial conc. of Cr(VI) Co (mg/L)	Equil. conc. of Cr(VI) C_e (mg/L)	Amount of Cr(VI) adsorbed x (mg)	Amount of Cr(VI) adsorbed per g of carbon x/m (mg/g)	log x/m	log C_e
FTSC Dose = 80	10	1.4	8.6	10.75	1.0314	0.1461
	20	4.4	15.6	19.50	1.2900	0.6434
	30	9.0	21.0	26.25	1.4191	0.9542
	40	14.0	26.0	32.50	1.5118	1.1461
	50	21.0	29.0	36.25	1.5590	1.3220
CAC Dose = 120	10	1.6	8.4	7.00	0.8450	0.2041
	20	5.4	14.6	12.60	1.0849	0.7323
	30	9.6	20.4	17.00	1.2304	0.9822
	40	14.6	25.4	21.16	1.3255	1.1643
	50	20.0	30.0	25.00	1.3979	1.3010

The logarithmic forms of the equation becomes:

$$\log (x/m) = \log K + 1/n \log C_e$$

Freundlich adsorption isotherm represents the relation between the amount of chromium adsorbed per unit mass of the adsorbent (x/m) and the concentration equilibrium (C_e). K and n are the constants representing the adsorption capacity and intensity of adsorption, respectively. The data obtained in this study fit in Freundlich adsorption isotherm (Figs. 4 and 5). The plot of log (x/m) *versus* log C_e for various initial concentrations is found to be linear indicating the applicability of classical adsorption isotherm to this adsorbate adsorbent system. The isotherm offers a full view of the relative efficiency of carbons over the entire range of concentrations studied. Thus in Figs. 4 and 5 the isotherm shows similar trend for adsorption of Cr(VI) on to the different carbons, indicating uniform adsorption over the entire range of concentrations.

Experiments were also conducted in order to understand chromium adsorption on activated carbon. The rate constant (K) was determined using Bhattacharya and Venkobachar equation[10].

$$\ln [1-U(t)] = -Kt$$

where U(t) = (Co - Ct) / (Co - Ce).

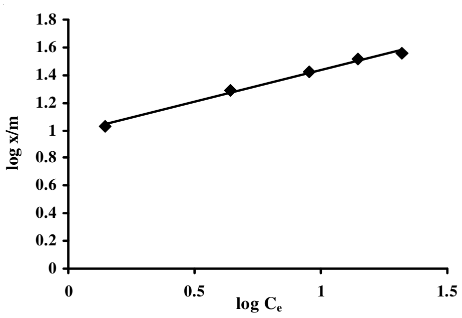

Fig. 4. Freundlich adsorption isotherm for Cr(VI) with FTSCC

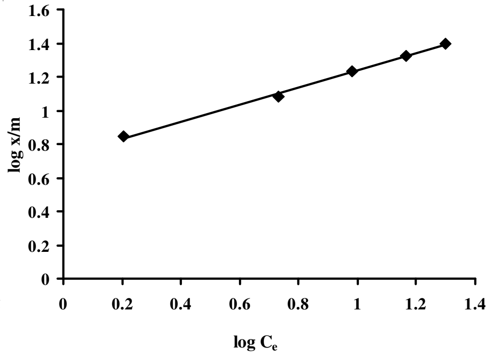

Fig. 5. Freundlich adsorption isotherm for Cr(VI) with CAC

Co, Ct and Ce are the concentration (mg/L) of adsorbate initially, at any time t and at equilibrium, respectively. The straight line plot of ln [1-U(t)] *versus* t indicates that the process follow first order kinetics. Kinetic studies were conducted for various initial concentrations of chromium and the overall rate constant for a given concentration was calculated from the slope of straight line. It is understood that the adsorption of chromium in aqueous system follows reversible first order kinetics when a single species is considered on a heterogeneous surface.

The two important physicochemical aspects for parameter evaluation of the sorption process as unit operation are the kinetics and the equilibria. Kinetics of sorption describing the solute uptake rate which in turn governs the resident time of sorption reaction is one of the characteristic defining the efficiency of sorption. Hence in the behaviour of this study, the kinetics of the chromium removal has been carried out to understand the behaviour of FTSCC (the low cost adsorbent). Concentrations of chromium over the range of 10-50 mg/L were attempted (Figs. 6 and 7). Using the conventional equations, the equilibrium constant Kc, forward and backward rate constant k_1 and k_2 were calculated and presented in the Table-3. From the values it is seen that the forward rate constants (k_1) for the removal of chromium are much higher than the backward rate constants (k_2) namely adsorption process for FTSCC and CAC. Further more, comparison of the over all rate constants 'k' for the removal of Cr(VI) under study by FTSCC are higher than that of CAC. Hence it is concluded that the removal of Cr(VI) by FTSCC is a faster process than by CAC. The values of the film coefficient in the range 10^{-8} cm^2/s indicate that the adsorption is controlled by the film diffusion process.

Conclusion

The activated carbon prepared by carbonization of FTSCC with acid process followed by thermal activation is found to be a good adsorbent for the removal of chromium(VI) from aqueous solution. It is showed that more than 90 % removal of chromium at pH 2.5 at optimum conditions. The values of adsorption capacity (k = 10.0) and intensity (n = 2.14) indicate the greater affinity for chromium by this

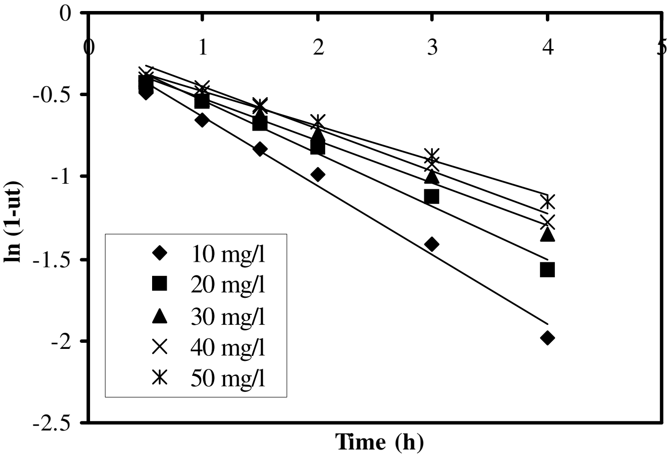

Fig. 6. Kinetic fits of Cr(VI) adsorption data for FTSCC

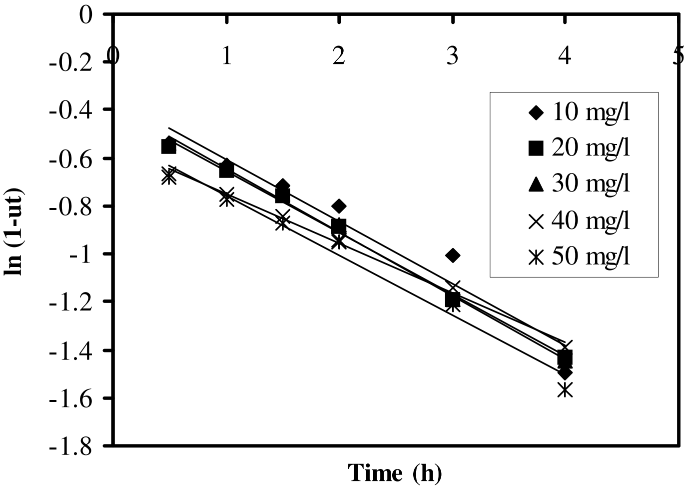

Fig. 7. Kinetic fits of Cr (VI) adsorption data for CAC

TABLE-3
RATE CONSTANT FOR THE REMOVAL OF Cr(VI) WITH FTSCC AND CAC

Adsorbent	Cr(VI) concentration (mg/L)	Overall rate constant $k = k_1 + k_2$ (h^{-1})	Forward rate constant k_1 (h^{-1})	Backward rate constant k_2 (h^{-1})
FTSCC	10	0.3552	0.3338	0.0214
	20	0.2500	0.2149	0.0351
	30	0.1976	0.1442	0.0534
	40	0.1886	0.1282	0.0604
	50	0.1506	0.0903	0.0603
CAC	10	0.1857	0.1819	0.0038
	20	0.2190	0.2014	0.0176
	30	0.2272	0.2020	0.0248
	40	0.1851	0.1332	0.0519
	50	0.2095	0.1403	0.0692

activated carbon. The low values for k_2 (desorption process) indicates that the adsorbed chromium remains almost stable on the adsorbent that can be recovered from the adsorbent using suitable regenerant. The adsorption of chromium on the activated carbon shows film diffusion process.

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