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Removal of Toxic Chromium(VI) by the Adsorption of Activated Carbons Prepared from Mahua Shells

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Removal of toxic Cr(VI) in aqueous medium was investigated using activated carbon adsorbents prepared from Mahua seed shells. The pH effect, concentration, adsorbent dosage and contact time period were studied in batch experiment. The removal of Cr(VI) was in general most effective at pH range 2.0–4.0. Activated carbons are prepared at 800 ± 50°C temperature. One is non-impregnated and the remaining three are impregnated with zinc chloride in 1 : 1, 1 : 2, 1 : 3 ratio. Important characteristics of activated carbons are also investigated. The data for all the adsorbents fit well to the Freundlich adsorption isotherm. The removal of Cr(VI) is around 97% was observed with 1 : 2 impregnated activated carbon at pH 3.0 whereas other adsorbents showed much lower activities.

Key Words: Adsorption, Cr(VI), Activated carbon, Activated Mahua carbon.

INTRODUCTION

There are two predominant forms of chromium, *i.e.*, Cr(III) and Cr(VI). Hexavalent form is more hazardous to biological activities.The treatment of chromium bearing effluents has been reported through several methods such as reduction .precipitation[1, 2], ion exchange, reaction with silica, electrochemical reduction, evaporation, reverse osmosis and direct precipitation. Most of these methods need high capital cost. Studies on the treatment of effluents bearing heavy metals have revealed adsorption to be highly effective, cheap and an easy method among the physico-chemical treatment processes[3]. Owing to the high cost and difficult procurement of activated carbon, efforts are being directed towards finding efficient and low cost adsorbent materials. A variety of low cost materials like fly ash[4], wood charcoal[5], lignite coal[6], rice husk carbon[7], saw dust[8, 9] and groundnut husk have been tried. Activated carbons prepared from agriculture wastes also proved as efficient adsorbent materials.

In the light of above, herein we report the preparation, characterization and adsorption capacities of activated carbons prepared from Mahua seed shells (*Madhuca indica*) for removal of Cr(VI).

EXPERIMENTAL

To assess the quality and performance of adsorbent and to avoid interference of other elements, an experiment was performed with the aqueous solution of Cr(VI) in doubly distilled. water. Synthetic Cr(VI) samples of various initial concentrations were prepared by dissolving $K_2Cr_2O_7$ in water. The activated carbons were prepared using the procedure[10]. Mahua seed shells (M) are waste materials. These shells are collected from oil mills and cleaned, dried, powdered and sieved through 150 microns. This powder is activated in muffle furnace at 800 ± 50°C for an hour (pyrolysis). Powder is chemically treated with zinc chloride and activated carbons such as 1:1, 1:2 and 1:3 mahua and zinc chloride are prepared.

Mahua shell powder and zinc chloride were taken and mixed with a small quantity of distilled water and kept for 24 h. Afterwards it was dried in an air oven at 100–120°C for 5 h, then transferred into a container which fits in another larger container, it was surrounded by sand on all sides and activated in muffle furnace at 800 ± 50°C for 1 h, cooled, washed with 0.25 M HCl and distilled water several times, dried, powdered and sieved through 150 microns.

Carbons non-impregnated and impregnated with $ZnCl_2$ in 1:1, 1:2, 1:3 ratio were activated by using the above procedure and used for the present study.

To study the adsorption capacities of these adsorbents, batch experiments were carried out. These are simple and effective to evaluate the basic parameters affecting adsorption. Synthetic samples of various initial Cr(VI) concentrations ranging from 10 to 40 mL of 0.01 M were taken separately in conical flasks. Suitable doses of activated carbon of 0.1 to 1.0 g were added. The system was equilibrated by shaking thoroughly on an electric shaker and kept for 0.5 h. The suspension was then filtered using Whatmann No. 41 filter paper and the filtrate was estimated by using hypo for residual Cr(VI) concentration in the solution. The effect of pH (1.0–8.0), effect of adsorbent dose, initial Cr(VI) concentration, contact time, temperature and rate kinetics were studied.

RESULTS AND DISCUSSION

Adsorption for Cr(VI) studies showed that 30 min time period is adequate to ensure equilibrium between Cr(VI) adsorbed and chromium left in the solution. Table A presents the important characteristics of different adsorbents that is non-impregnated and impregnated with zinc chloride.

TABLE-A
CHARACTERISTICS OF ADSORBENTS

Adsorbent	% Moisture	% Volatile matter	% Ash
Non impregnated activated carbon	2	10.9	11.0
Impregnated activated carbon:			
1:1	17	5.2	9.80
1:2	15	6.0	13.0
1:3	17	6.0	15.0

Effect of Adsorbent Dose

For all these runs, initial Cr(VI) concentration was fixed at 10 mL of 0.01 M, and amount of adsorbent dose was varied from 0.1 to 1.0 g. pH was adjusted to 4.38. The results showed that the removal of Cr(VI) was effective when 1:2 impregnated activated carbon was used as an adsorbent (Table-1 and Fig. 1). Results revealed that the percentage removal of Cr(VI) by increasing adsorbent dose from 0.1 to 0.5 g was effective initially and later adsorbance efficiency decreased. Removal was around 70%.

TABLE-1
EFFECT OF ADSORBENT DOSE

Wt. of activated carbon	1:1 (M:$ZnCl_2$)	1:2 (M:$ZnCl_2$)	1:3 (M:$ZnCl_2$)
0.1	10	10	50
0.2	25	35	50
0.3	35	40	40
0.4	40	55	30
0.5	45	70	30
0.6	4	—	10
0.7	3	—	—
0.8	2	—	—

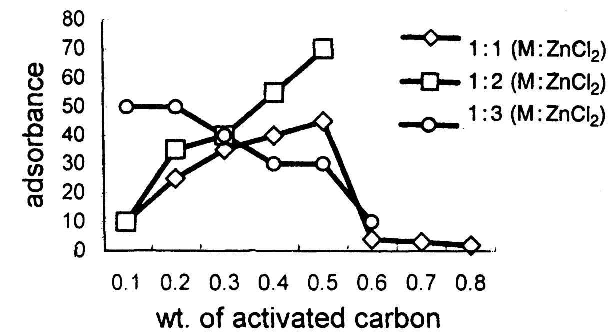

Fig. 1 Effect of adsorbent dose

Effect of pH

These runs were undertaken at constant initial Cr(VI) concentration of 25 mL of 0.01 M in 50 mL and adsorbent dose 0.5 g/50 mL. The results indicate that among four adsorbents studied, 1:2 M:$ZnCl_2$ has the maximum capacity for Cr(VI) removal at pH range 2.0–4.0 (98%) and pH 5.0 onwards adsorbance decreases (Table-2). The observation showed that the adsorption capacity of 1:2 (M:$ZnCl_2$) adsorbent is good in the pH range 2.0–4.0 but at natural pH (4.28) it is 70%.

The reason for more adsorption capacity observed at low pH values may be due to large number of H^+ ions present at low pH values which in turn neutralize the negatively charged adsorbent surface, thereby reducing hindrance to the diffusion of dichromate ions.

TABLE-2
EFFECT OF pH

pH	Non-impregnated	1:1 (M:$ZnCl_2$)	1:2 (M:$ZnCl_2$)	1:3 (M:$ZnCl_2$)
1	3.5	69.0	80.8	82.7
2	8.5	88.5	94.2	94.2
3	8.5	88.5	94.2	94.2
4	8.5	94.2	94.2	88.5
5	4.8	48.0	63.5	48.1
6	5.0	14.8	19.2	—

At higher pH, reduction in adsorption may be possible due to abundance of OH^- ions causing increased hindrance to diffusion of dichromate ions. Other workers have also reported similar observation. For further studies pH 3.0 solutions were selected. Fig. 2 shows the effect for pH of four adsorbents.

Effect of Initial Concentration of Cr(VI)

Removal of Cr(VI) as a function of its increased initial concentration at pH 3.0 using 1:1, 1:2 and 1:3 M:$ZnCl_2$ activated carbons was investigated. 1:2 activated carbon (M:$ZnCl_2$) showed 98% of adsorption at lower concentrations. 10, 15, 20, 25, 30, 35, 40/50 mL samples of 0.01 M Cr(VI) and 0.5 g/50 mL activated carbon were taken. The percentage removal of Cr(VI) as a function of its increased initial concentration at pH 3.0 is shown in Fig. 2 and Table-3. The impregnated activated carbon 1:2 and 1:3 showed maximum adsorption (98%).

TABLE-3
EFFECT OF INITIAL CONCENTRATION AT pH 3

Concentration	1:1 (M:$ZnCl_2$)	1:2 (M:$ZnCl_2$)	1:3 (M:$ZnCl_2$)
5	67.9	83.0	53.9
10	86.8	89.8	75.0
15	93.0	93.3	94.9
20		95.0	97.8
25		98.0	97.7

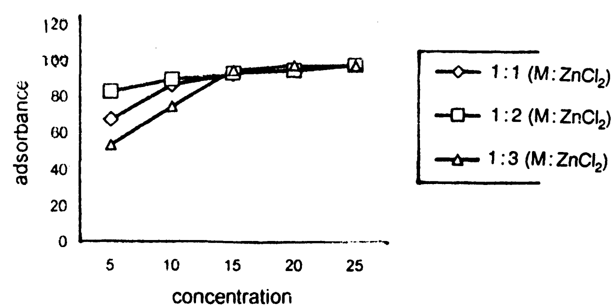

Fig. 2. Effect of initial concentration at pH 3

Effect of Temperature

The temperature dependence of adsorption process is of complex nature. Thermodynamic parameters like heat of adsorption and the energy of activation play an important role in predicting the adsorption behaviour and both are strongly temperature-dependent. Initial concentration of hexavalent chromium was 10 mL of 0.01 M in 50 mL and adsorbent dose was 0.5 mg/50 mL. Effect of temperature on adsorbents was constant up to 30–40°C and it decreased later. Similar trends were observed with 1:1 and 1:2. The phenomena of decrease in activity with temperature rise may be explained on the basis of the overall effects of the temperature on the Cr(VI) adsorbent bond, the water-adsorbent bond.

Rate Kinetics

The adsorption studies conducted at fixed initial concentration and varying adsorbent dose were fitted to the linearised Freundlich adsorption isotherm which of the form

$$\log [x/m] = \log K + 1/n \log C.$$

where x/m is the amount of Cr(VI) adsorbed per unit mass of adsorbent (mg/g) and C is the equilibrium concentration of aqueous solution. K is a constant which is a measure of adsorption capacity, and 1/n is a measure of adsorption intensity. The values of constant K and 1/n for different adsorbents were calculated. Since the values of 1/n are less than 1, it indicates a favourable adsorption. 1:1, 1:2 and 1:3 activated carbons have 0.875, 0.13 and 2.6 1/n values respectively. 1:2 carbon's 1/n value indicates its greater activeness when compared to other adsorbents and comparable with fly ash[4], activated GHC[11], bagasse ash[12], raw bagasse[12] (Tables 4–6).

TABLE-4
RATE KINETICS

Log c	Log x/m
1.10	1.86
1.19	1.81
1.26	1.77

TABLE-5
RATE KINETICS

Log c	Log x/m
0.80	1.87
0.93	1.84
1.10	1.81
1.26	1.76

TABLE-6
RATE KINETICS

Log c	Log x/m
1.0	1.03
1.1	0.08
1.6	0.05

Conclusions

Based upon the investigations we can say that the 1:2 ($M:ZnCl_2$) impregnated activated carbons are effective adsorbents for Cr(VI). The percentage removal of Cr(VI) at pH 3.0 and 4.28 are 98% and 70% respectively.

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