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ADSORPTION STUDIES ON REMOVAL OF Cr (VI) FROM AQUEOUS SOLUTION USING SILK COTTON HULL CARBON

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ABSTRACT

Activated carbon prepared from silk cotton hull carbon (SCHC) was used to remove Cr(VI) from aqueous solutions by adsorption technique under varying conditions of agitation time, metal ion concentration, adsorbent dosage and pH. Adsorption followed both Langmuir and Freundlich isotherm models. The adsorption capacity was found to be effective with the particle size of 125-250mm at room temperature (30±2°C) and an initial pH of 3±0.2.

INTRODUCTION

Heavy metals in the environment are of global concern due to their non-degradability and biomagnification. Among several heavy metals, chromium compounds are used extensively in industrial processes such as electro plating, leather tanning and in the manufacture of paints, dyes, paper, explosives and ceramics. Hexavalent and trivalent chromium possesses carcinogenic properties (Hueper and Payne, 1962). Large doses of hexavalent chromium lead to corrosive effects in the intestinal tract and to nephritis. Many conventional methods can be adopted for the removal of Cr from wastewater. However

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the methods are expensive in Indian context where economy plays a major role. This resulted in a quest of low-cost, non-conventional adsorbents for heavy metal removal such as coir pith carbon, coconut saw dust carbon (Selvi *et al*. 2001), and peanut hull carbon (Periasamy & Namasivayam 1995).

This study deals with the use of activated carbon prepared from silk cotton hull as an adsorbent for the removal of Cr (VI) from aqueous solution. Silk Cotton hull is dumped in and around silk cotton processing industries and available as large mass of causing disposal problem in industries. Coimbatore is the place where more silk cotton processing industries are present, ranking second among the countries. The main aim of this work was to evaluate the feasibility of using silk cotton hull carbon for Cr (VI) removal.

MATERIALS AND METHODS

Adsorbent

Silk Cotton Hull (SCH) obtained from silk cotton processing unit was cut into small pieces, dried in sunlight until the moisture was partially evaporated and was further dried in a hot air oven at 600C for 24 h. The dried material was chemical activated by treating with 50% sulfuric acid and ammonium per sulphate (0.5%) with constant stirring. The charred material was kept in hot air oven at 100 ± 50^{0}C for 24 hours and washed with double distilled water. Then the material was soaked in 5% sodium bicarbonate solution and allowed to stand overnight to remove any residual acid, washed with distilled water until the pH of the adsorbent attains a pH of 3 + 0.2 and dried in a hot air oven at 100 + 5oC for 12 hours. The dried material was sieved to get the particle size of 125 - 250 µm and was used in this study.

Adsorbate

1000 mg/L of Cr (VI) was prepared by dissolving 2.8287 g of potassium dichromate in double distilled water. The stock solution was diluted with distilled water to obtain the required standard solutions.

Batch mode adsorption studies

The working solution of 10, 20, 30, 40 mg/L of Cr (VI) was prepared from stock solution. Batch mode adsorption studies were carried out with 250 mg of the adsorbent and 50mL of Cr (VI) solution of desired concentration at a pH of 3.0±0.2, agitated at 120 rpm in a mechanical shaker at room temperature. The adsorbate solution was separated from the adsorbent by centrifugation at 500 rpm and estimated spectrophotometrically at 540 nm using diphenyl Carbazide (APHA, 1980). The effect of carbon dosage on percent removal of Cr (VI) was studied with solutions of 30 and 40 mg/L for particle size 125 - 250µm. Effect of pH on Cr (VI) removal was studied for metal ion concentration of 10, 20mg/L using 250mg of carbon dosage. Langmuir isotherm study was carried out with different initial concentration of Cr (VI) from 5 to 30mg/L, while maintaining the adsorbent dose at 250mg/50mL. Desorption studies was carried out to confirm the adsorption mechanism proposed above and to recover the metals from the adsorbent using 0.25 to 1.75 N sodium hydroxide solution.

RESULTS AND DISCUSSION

Adsorbent Characterization

Characteristics of activated carbon prepared from silk cotton hull are presented in Table 1. The determined surface area of silk cotton hull activated carbon (SCHAC) was 228 m2/g and is comparable to various low cost adsorbents namely, peanut hull carbon (Periasamy and Namasivayam, 1996) (208 m2/g), eichhornia (Shekinah *et al*. 2002) (200 m2/g), cassava (Rajeshwari *et al*. 2001) (200 m2/g) and coconut tree saw dust carbon (Selvi *et al*. 2001) (325 m2/g). The moisture content of the carbon was found to be 2.4% (Table 1). The phenol adsorption capacity and decolorizing power were 11.2 and 22.5 mg/g respectively which indicates that the carbon prepared by acid activation method has good adsorption capacity. The surface morphology of Silk cotton hull activated carbon (SCHAC) was visualized via scanning electron microscopy (SEM), the corresponding SEM micrographs being obtained using a JSM-840 JEOL microscope of JEOL Techniques LTD, Japan at 2000x magnification (Fig 1). Examination of SEM micrographs of the SCHAC particles showed rough areas of the surface of the carbon and the microspores were identifiable. The activation process of SCHAC by adopting sulphuric acid treatment leads to corrode the surface of carbonaceous material and introduce micro, macro and mesopores.

Effect of agitation time and initial metal ion concentration on Cr (VI) removal

The effect of agitation on the percentage removal of Cr (VI) from aqueous solution by activated carbon prepared from silk cotton hull is shown in Fig (2). The removal rate was rapid initially and then slowed down gradually until it attained equilibrium beyond which there was no significant increase in the rate of removal. The equilibrium was attained with in 180 min for all the concentrations studied (10 to 40 mg/L). The curves obtained were single, smooth and continuous till the saturation of Cr (VI) onto activated carbon surface.

Adsorption Kinetics

The rate constants of Cr (VI) adsorption onto SCH carbon follows first order rate expression given by Lagergren.

Where q & qe are the amount of metal ion adsorbed by the adsorbent at time 't' and at equilibrium time respectively. Kad is the rate constant of adsorption in 1/min. The linear plots of log10 (qe-q) Vs t for different metal ion concentrations indicate applicability of the above equation for the adsorption of Cr (VI) ion onto activated carbon. The values of kad were calculated from the slope of the linear plots and are presented in Table 2

Effect of carbon dosage on percent removal

The effect of carbon dosage on percent removal of Cr (VI) is shown in Fig (3). When the carbon dosage increases, the percent removal also increases. It was found that 100% removal of 30 & 40 mg/L of Cr (VI) require 450 and 550 mg of carbon respectively.

Adsorption Isotherm

The Langmuir isotherm can be applied for adsorption equilibrium of Cr (VI) onto SCH carbon.

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}$$

Where, Ce is the equilibrium concentration (mg/L). qe is the amount of Cr (VI) adsorbed (mg/g), Q0 and b are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. The linear plot of Ce/qe Vs Ce shows that the adsorption follows Langmuir isotherm model (Fig. 4). The value of Q0 & b calculated for 10mg/L concentration were,

Q0 = 30.30 mg/g
b = 0.420 1/min

Langmuir isotherm can be expressed in terms of dimensionless separation factor or equilibrium parameter (Mckay *et al*. 1980) and can be written as,

$$R_L = \left(\frac{1}{1 + bC_0} \right)$$

Where,
C0 is the initial Cr (VI) concentration in mg/L and b is the Langmuir constant (L/mg).

Table 1. Characteristics of Activated Carbon

pH (1% Solution)	7.69
Moisture content (%)	2.86
Ash content (%)	1.987
Decolourising power (mg/g)	22.5
Phenol adsorption capacity (mg/g)	11.2
Ion-exchange capacity (milli equi/g)	0.0145
Apparent density (g/mL)	0.42
Water soluble matter (%)	2.0
Acid soluble matter (%)	7.0
Surface area (m2/g)	228.0

Table 2. Lagergren Rate Constant for Cr (VI) Adsorption

Conditions
pH - 3 ± 0.2
Carbon dosage - 250 mg/50mL
Particle size - 125 – 250 mmin

Cr (VI) Concentration mg /L	Rate constant K_{ad} (1/ min)
10	0.0216
20	0.0159
30	0.0140
40	0.0212

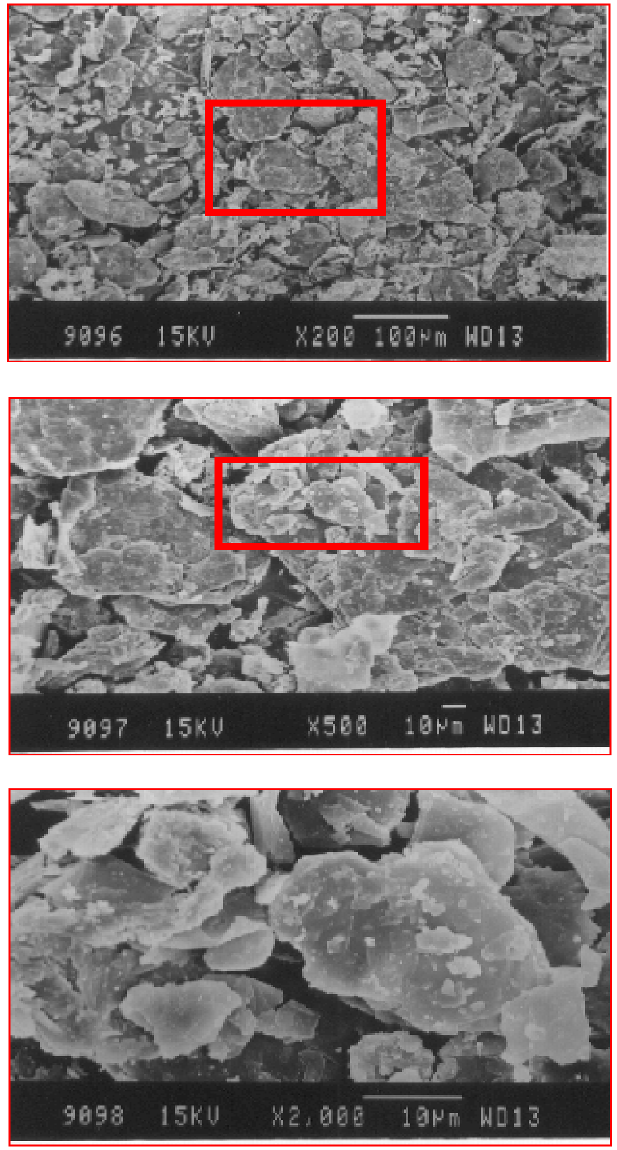

Fig 1. SEM photograph of Silk Cotton Hull Activated Carbon (SCHAC) at various magnifications (x200, x500 and x2000) silk cotton hull carbon

The type of isotherm can be revealed by RL value.

RL value	Type of isotherm
RL >1	Unfavorable
RL= 1	Linear
0<RL<1	Favorable
RL=0	Irreversible

The linear form of Freundlich equation can be given by

Where, x is the amount of Cr (VI) adsorbed at equilibrium (mg), m is the

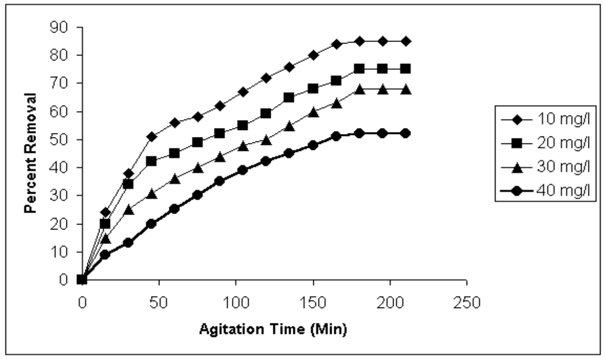

Fig. 2. Effect of Agitation time on Cr (VI) absorption

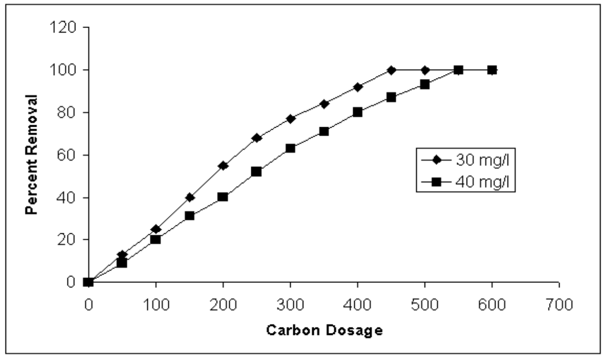

Fig. 3. Effect of carbon dosage on Cr (VI) absorption

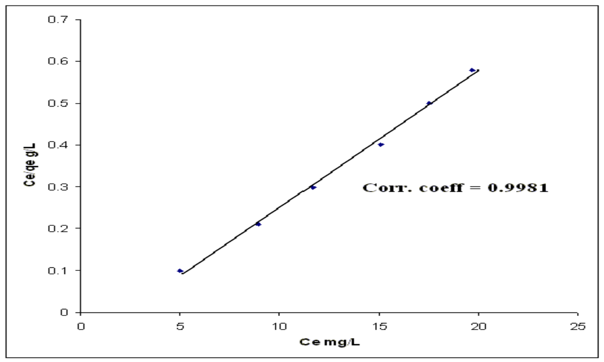

Fig. 4. Langmuir plot for Cr (VI) absorption

weight of adsorbent used (mg), Ce is the equilibrium concentration of Cr(VI) in solution (mg/L). kf and n are constants. Linear plot of log x/m Vs log Ce shows that the adsorption follows Freundlich isotherm (Fig.5). The Freundlich constants kf and n are found to be 3.588 and 0.5263 respectively for the concentration of 10mg/L.

Effect of pH on Cr (VI) removal

Effect of pH on Cr(VI) removal is shown in Fig. (6). Adsorption decreases

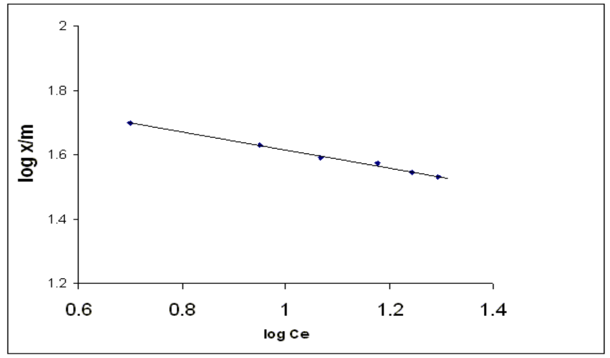

Fig. 5. Freundlich plot for Cr (VI) adsorption

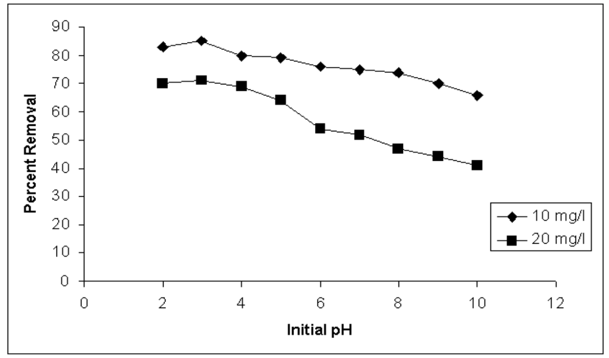

Fig. 6. Effect of pH on Cr (VI) absorption

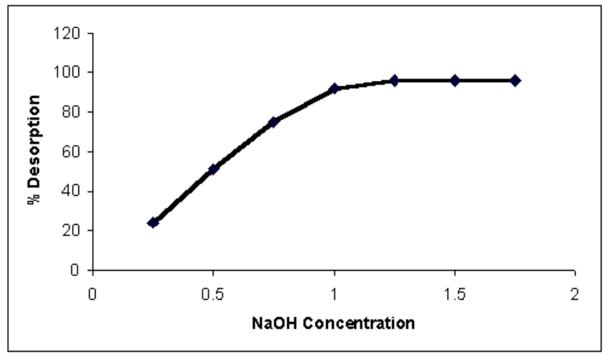

Fig. 7. Effect of NaOH concentration on desorption of Cr (IV)

with increase in pH. Lower adsorption of Cr(VI), at alkaline pH is probably due to the presence of excess of OH- ions competing with the metal ions for the adsorption sites. The highest percent removal was possible at an initial pH of 3±0.2.

Desorption Studies

Attempts were made to degenerate metal ion from the laden carbon using various strengths of NaOH (0.25 to 1.75 N). Desorption data indicates the mechanism of adsorption is the ion-exchange process and the complete regeneration of adsorbate and adsorbent are possible. Fig. 7 shown the effect of NaOH on Cr (VI) adsorption

CONCLUSION

The activated carbon prepared from silk cotton hull carbon can be used for the removal of Cr (VI) from aqueous solution effectively. The adsorption depends on solution pH, initial metal ion concentration, and carbon dose. The adsorption followed both Langmuir & Freundlich isotherm models. Desorption data indicates the mechanism of adsorption is the ion-exchange process and the complete regeneration of adsorbate and adsorbent are possible

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