Preparation of Activated Carbon for the Removal of Cr (VI) from Aqueous Solutions

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ABSTRACT

Activated carbon prepared from sulphuric acid treatment followed by thermal activation of cotton seed carbon is investigated for the removal of Cr (VI) ione from solutions. The influence of various factors such as agitation time, pH & carbon dosage on the adsorption capacity has been studied . Freundlich equation could be used to interpret adsorption data. Sorption kinetics has indicated that reversible first order kinetics model could be applied with diffusion as the controlling mechanism.

Key words : Cotton seed carbon, Cr(VI) adsorption, Freundlich method.

1. Introduction:

Water is considered as a most useful compound, which is abundantly available on this earth. It is not only used for the human existence but also used extensively for many of the industrial manufacturing process[1].The heavy metals present in these wastewaters from factories are posing serious problems in recent years; traces of heavy metal such as Hg, Cd, Pb, AS, Co, Mn & Cr have been identified as deleterious to aquatic aqueous system & human health[2]. Chromium compounds are used extensively in industrial process such as metal pickling, electroplating, & aluminum anodizing, leather caning and in ceramics[3]. Chromium generally occurs in hexavalent and in trivalent form. Chromium is capable of causing skin disorders & liver damage[4]. These harmful effects of Cr (VI) ions necessitate its removal from wastewaters before release into streams.

Activated carbons from cheaper & readily available materials such as rice husk[5], coconut shell[6] etc, have been applied for the removal of Cr (VI) from wastewaters. In this connection it was proposed to make a carbon from cottonseed[7], a seed variety, utilized for the removal of Cr (VI) from water and wastewater[8].

Experimental

50 g of dried cottonseeds treated with 200 g of sulphuric acid and then kept in an air oven maintained at 140-160^{0}c for a period of 24 hours. The product was washed with water to remove sulphuric acid and dried at 110^{0}c. After the acid process was completed the material was thermally activated using muffle furnace maintained at 800^0 c . This carbon taken in the size range (20-50 mesh) CSC was evaluated for chromium (VI) removal. After the activation period the carbonized sample was transferred in to a beaker & covered it immediately with a watch glass to avoid the formation of ash. The process was repeated till the required amount of carbon obtained. This carbon was used for batch studies & kinetic experiments. The carbon characteristics were found out using ISI-877 procedures & given in table -1. It could be seen that this carbon contains sufficient bulk density, phenol number, and surface area & exchange capacity so that it can be used for adsorption purposes.

Table 1   Carbon characteristics (CSC)

S. No.	Description	Results
1	Bulk density, g/cc	0.54
2	Moisture content, %	12.32
3	Ash, %	8.00
4	Matter soluble in water, %	2.37
5	Matter soluble in acid, %	5.27
6	Decolorizing power, mg/g	0.15
7	Phenol number	15
8	Ion exchange capacity milli equivalent / g	0.294
9	Surface area sq.m/g	545.6
10	Iron contents, %	1.15
11	pH	6.50

Batch mode studies;

A stock solution of Cr(VI) ions (50mg/L) was prepared by dissolving 0.1414g of potassium dichromate in water and diluting to one liter. Appropriate volumes of stock solution were suitably diluted with water to obtain a concentration of 20 mg /L for batch experiment & 0.2g of Carbazide (1,5- dipheryl carbazide) was dissolved in 100mL of isopropyl alcohol. To this 100mL of 3.6N Sulphuric acid solution was added slowly with constant stirring. The solution was kept in the refrigerator. Experiment have been conducted with 100mL of 10mg/L of Cr(VI) ions under investigation were taken in the bottles and equilibrated for specific periods of time in a rotary mechanical shaker. At the end of the equilibrated period, the solution was filtered; using a G3 crucible if necessary and the concentration of respective ions were established by spectrophotometry.

Results and discussion:

Batch experiments were performed to establish various parameters for the removal of chromium (VI) from aqueous solutions. Experiments were carried out using 100mL of solution containing 10mg of Cr (VI) /L adjusted to pH ranges 1.0-10.0 contained in 300ml stopper bottles; after adding required amounts of carbon. The solutions were equilibrated in a mechanical shaker. The equilibrated solutions were filtered using G3 crucible, if necessary and the amount of hexavalent chromium present in the solution was determined. From these data chromium taken up by the carbon was established. The performance of cottonseed carbonized with sulphuric acid after thermal activation at 800^0c was taken for experimental purposes. This carbon taken in the size range (20-50mesh) (CSC) was evaluated for chromium (VI) removal.

Effect of equilibrium time

In order to find out the optimum equilibration time, experiments were carried out using 0.1g of carbon and 100mL chromium (VI) solution were analyzed and a chromium (VI) removed was established. The results are shown in Fig -1. From which it is clear that 1.5 hours of equilibration time is sufficient for maximum chromium (VI) removal by CSC. However it was decided to maintain equilibration time of 3 hours in all subsequent experiments.
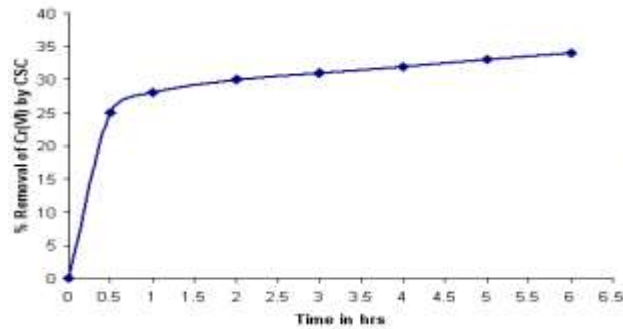
Fig.1: Effect of Time for the Removal of Cr (VI) of Concentration 10mg/L-Carbon Dose 100mg/100mL; pH: 5.0

Effect of pH

In order to find out the optimum pH for the maximum chromium (VI) removal ,experiments were carried out by varying the pH of the solution over the range 1.0-10.0 after the equilibrating for 3 hours .The solutions were analyzed and hexavalent chromium removed were established. The results are shown in fig-3. The amount of carbon used was 100mg/ 100ml of the solution; it is clear from the plot that maximum removal of chromium (VI) occurred, over the pH range 1.0-2.0 for CSC. The removal of chromium (VI) falls of gradually over the pH range 3 to 5 and practically remains constant from pH 5.0 to 9.0.
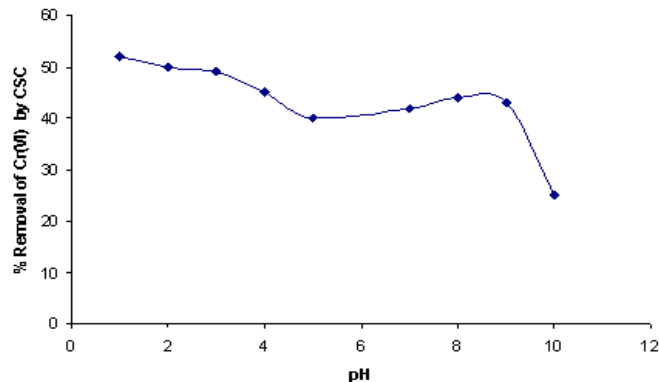

Fig.2: Effect of pH on Adsorption of Cr (VI) of Concentration 10mg /L-Time: 3hrs: Carbon Dose 100mg/100mL; pH: 5.0-9.0

Effect of carbon dosage

In order to find out, the optimum carbon dose required for chromium (VI) removal experiments were carried out with 100ml chromium (VI) solutions of 10mg/lit over the pH range1.0-7.0. By adding varying amounts of carbon ranging from 0.05g-0.6g. Hexavalent chromium removed in each instance was established after equilibrating the solution for 3 hours. The results are given in figures 3-5.
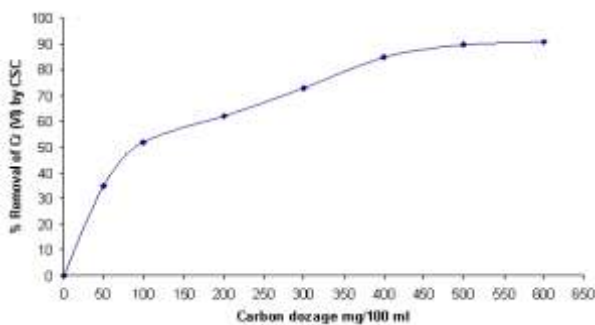

Fig: 3 Effect of Carbon Dosage on Adsorption of Cr (VI) Of Concentration 10mg/L- Time 3Hrs; pH : 1
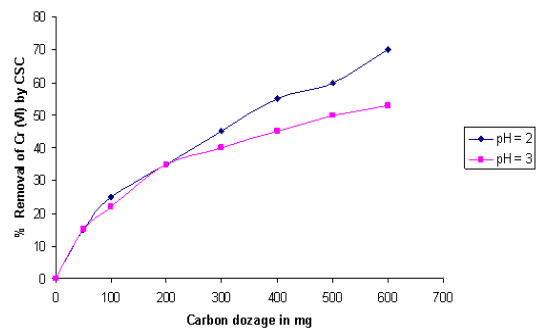
Fig: 4   Effect of Carbon Dosage on Adsorption of Cr(VI) of Concentration 10mg/L-time 3Hrs ; pH :2 & pH: 3
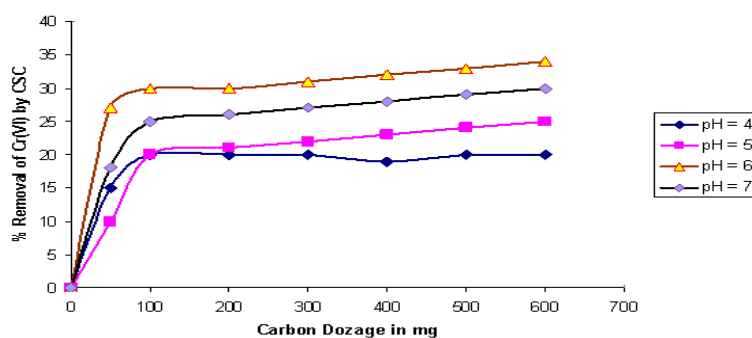
**Fig: 5   Effect of Carbon Dosage on Adsorption of Cr (VI)
Of Concentration 10mg/L- Time 3Hrs; pH : 4 to 7**

It could be seen that at pH 1.0, a minimum 0.5g of carbon is required for a maximum removal of 95% of chromium (VI)/ 100ml of the solution. At pH 2.0, 0.6g is required per 100ml to effect a removal of 75% of chromium (VI). Whereas pH 3.0 a further reduction in the chromium (VI) removal occurred, of 0.5g per 100ml. However, at pH 4.0-7.0 a chromium (VI) removal more or less remained constant to extent to an extent 20-30% only and minimum carbon dosage of 0.19 is required to effect removal 20%. From the above experimental results, it could be inferred that as the pH conditions is lowered, the minimum carbon dosage required for the maximum Cr (VI) removal is also increased which suggest that a part of the Cr (VI) may be undergoing is reduction process to   Cr (III) and this fact explains that Cr(VI) removal at lower pH condition is controlled by proton to Cr(VI) ratio.
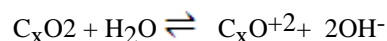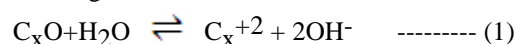
Mechanism of Cr (VI) Removal

In the case of Hexavalent chromium, at low pH conditions (>2.0), Chromic acid and dichromate ions are the predominate species and between pH 2.0 and 6.0 dichromate ions are the major species present in aqueous solution. At pH conditions >6.0, conversion of dichromate to chromate ions occur rapidly, though the process actually starts at pH>4.5 [9]. In other words, Chromate ions are the major species available at high pH condition (>8.0).

In the case of trivalent chromium, positively charged hydrated species occurs in the pH ranges 0-2.5. Over the pH ranges 4.0-6.0 the positive charge on the hydrated species decreases and eventually hydrated chromium species appears at pH conditions greater than6.0.

According to Shilov, Shatunovska, Chmutov[10] and Frumkin[11] groupings such as C_XO or C_XO_2 were formed on the surface of carbons during the activation of raw coke materials and cellulosic materials such as waste organic matter during the carbonization process. The existence of surface oxides should be considered as a primary product of the interaction between carbon and oxygen that is capable of being subsequently decomposed in to ultimate gaseous products of combustion-carbon monoxide and carbon dioxide. It has been reported that surface oxides participate in the adsorption of strongly ionized acids and bases as well as in the hydrolytic adsorption of inorganic salts[12, 13].
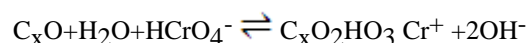
Studies made by Frumkin on carbon have shown that carbon acts like a gas electrode. The absorbed hydrogen in the presence of water formed hydronium ions that readily exchanged for other cations present in the solution phase. The adsorbed oxygen in the presence of water was transformed in to hydroxyl ions in natural or alkaline environment. As a result of this reaction, hydroxyl ions were produced and the pH of the solution was increased. The OH- ions were held at the carbon surface by electrovalent forces and thus facilitated the exchange with other anions.

$$C_XO + H_2O \rightleftharpoons C_X^{+2} + 2OH^- \quad ---------(1)$$

$$C_XO2 + H_2O \rightleftharpoons C_XO^{+2} + 2OH^-$$

Based upon the above reaction, Huang and Wu[14] proposed a mechanism of Cr (VI) adsorption from solution maintained at pH<6.0. Since dichromate ions are the predominant species under these conditions, its interaction with carbon surface was expressed as,

$$C_X^{+2} + HCrO_4^- \rightleftharpoons C_XOH_3Cr^+ \quad ------(2)$$

$$C_XO^{+2} + HCrO_4^- \rightleftharpoons C_XO_2HO_3Cr^+$$
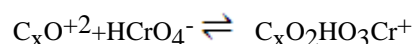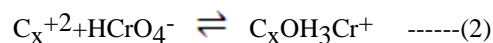
An overall reaction scheme was obtained by combining equations (1) and (2).

$$C_XO + H_2O + HCrO_4^- \rightleftharpoons C_XOHO_3 Cr^+ + 2OH^- ------ (3)$$

$$C_XO + H_2O + HCrO_4^- \rightleftharpoons C_XO_2HO_3 Cr^+ + 2OH^-$$

Freundlich Adsorption Isotherm

The Freundlich adsorption equation is the widely used mathematical description of adsorption in aqueous systems. The equation is expressed as[15],

$$X/m = K.C_e^{1/n} \qquad ……….1$$

Where

X = the amount of solute adsorbed

M= the weight of adsorbent

Ce = Equilibrium concentration of the solute

K, 1/n = Constants characteristics of the system.

The Freundlich equation is an empirical expression that encompasses the heterogeneity of the surface and the exponential distribution of sites and their energies.

For linearization of data, the Freundlich equation is written in logarithmic form,

$$Log\ x/m = log\ K + 1/n\ log\ C_e \qquad …2$$

Plotting log x/m Vs Ce, a straight line is obtained with a slope of 1/n, and log k is intercept of log x/m at log Ce = 0 (Ce=1). The value of 1/n obtained for absorption of the most organic compound by activated carbon is less than 1.Steep slopes of 1/n close to 1 indicate high adsorptive capacity at high equilibrium concentration that rapidly diminished at lower equilibrium concentrations covered by the isotherm. Relatively flat slopes i.e., 1/n<<1 indicate the adsorptive capacity is only slightly reduced at lower equilibrium concentrations. As the Freundlich equation indicated the adsorptive capacity (or) loading factor on the carbon, x/m is a function of equilibrium concentrations of the solute. Therefore, higher capacities are obtained at higher equilibrium concentrations.

The Freundlich equation can be used for calculating the amount of activated carbon. Required to reducing any initial concentration (Co) to a predetermined final concentration (Ce) by substituting (Co-Ce) for x in equation (2),

$$Log([Co-Ce]/m) = logK + 1/nlogCe \qquad --------3$$

Comparison of different activated carbons for the removal of different compounds or removal by the same carbon can be made using equation (3).

In order to establish the adsorption capacity of this carbon (CSC) experiments were conducted with different initial concentrations of Cr(VI) over the 10-60 mg/1 using both distilled water and tap water. The pH was maintained at 1.0-2.0. The amount of carbon added was 1g/1000 ml and the Solution was equilibrated for a period of 24 hrs. At the end of the equilibration, the solutions were analyzed and hexavalent chromium removed was established. From the data, the amount of Cr

(VI) removed per unit weight of carbon was calculated for all the concentrations of Cr (VI) under study (x/m).

The log values of the calculated quantities were plotted against the log of concentrations of Cr(VI) remaining in the solution(Ce) for this carbon. The plots are represented in the fig 6 and fig 7. The straight time nature of the plot indicated that the process followed Freundlich adsorption type. It could be seen from the graph 11 that at pH 1.0 the adsorption isotherm of Cr(VI) in distilled water solution occurs at a lower level when compared with Cr(VI) at tap water. It could be stated that at pH 1.0, the dichromate anion formed may be effectively removed by Ca and Mg present in the tap water with the result the adsorption isotherm drawn for Cr (VI) removal occurs slightly at elevated level when compared with distilled water. At pH 2.0 the Chromium (VI) adsorption isotherm for distilled water occurs at and elevated level than the adsorption isotherm drawn for tab water. At pH 2.0, it is assumed that most of the Cr(VI) that may be available in the form of dichromate ion, there by removal of Cr(VI) by the Ca and Mg ions in the form of calcium dichromate and magnesium dichromate might have been reduced.
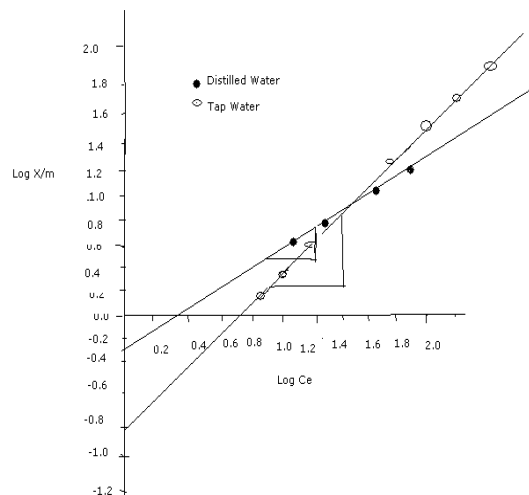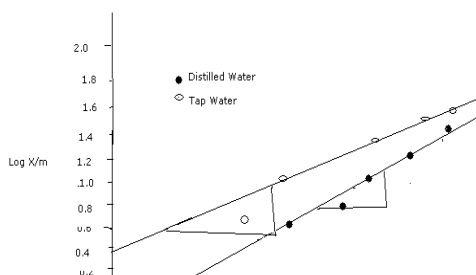

Fig.6: Freundlich Adsorption Isotherm for the Adsorption of Cr (VI)   ; Time: 10Hrs: pH: 1

Fig.7: Freundlich Adsorption Isotherm for the Adsorption of Cr (VI) ; Time: 10Hrs: pH: 2

The k value of adsorption equation for all the chromium (VI) concentration under study for distilled and tap water were obtained from the intercept on the x/m axis. The sorption intensities 1/n were obtained for (CSC) from the slope of the straight-line curve.

The Freundlich equations in the case both distilled water and tab water written as follows.

At pH 1.0

For distilled water $x/m = 0.5 \times C^{1.55}$

For tap water $x/m = 0.15 \times C^{1.17}$

At pH 2.0

For distilled water $x/m = 1.74 \times C^{0.62}$

For tap water $x/m = 0.52 \times C^{0.75}$

According, the sorption capacities of distilled water and tap water are worked out to be 0.5 mg/g and 0.15 mg/g respectively. However at
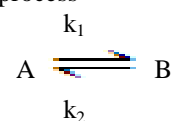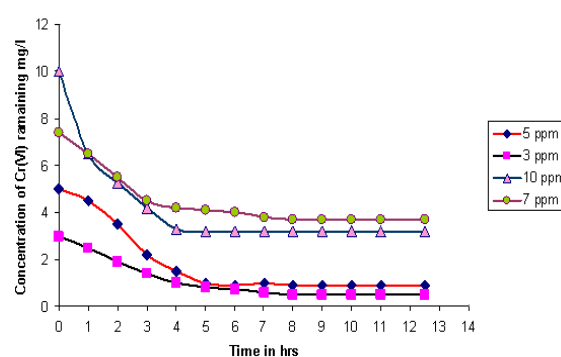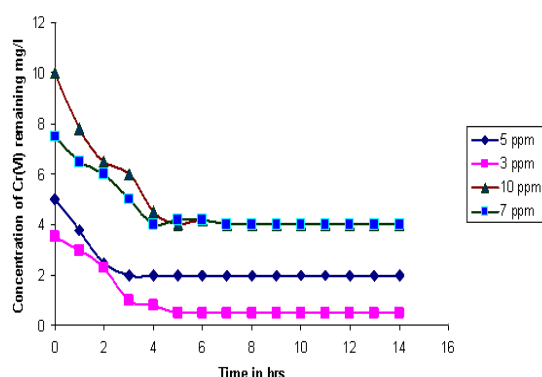
pH 2.0 at sorption capacities are worked out to be 0.42 and 0.09 respectively for distilled and tap water. A very low amount of adsorption capacity at pH 1.0 suggest that most of the Cr(VI) removal process may subjected to the reduction of Cr(VI) to Cr(III) on carbon surface.

Kinetic Studies

The two important physicochemical aspects for the evolution of the sorption process as a unit operation are the kinetics and the equilibria of sorption. The solute uptake rate and the residence time during which the maximum sorption takes place are some of the important characteristics defining the efficiency of sorption.

The sorption of the heavy metals from liquid phase to solid phase can be considered as a reversible reaction with equilibrium being established between the two phases. Since one solute is generally involved in the adsorption process, a simple first order reactions kinetic model [16] was used to establish the rates of reaction.

For a reversible process

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

Where k_1 = forward reaction rate constant

k_2 = backward reaction rate constant

By knowing the values of K and Kc,

It is possible to calculated k_1, k_2. Using the expression (6)

$$K = (k_1 + k_2) = k_1 + k_1/Kc = k_1 (1 + 1/K_c) \quad -----(6)$$

First Order Kinetic Fit for the Adsorption of Cr (V) on CSC

In order to understand the kinetics of adsorption process[17], experiments were carried out pH 1.0-2.0 with CSC using 100 ml solutions containing the metal ion understudy in the range 3 - 10 mg/1.A solution were taken in 300 ml bottles and to each, 0.1 of CSC was added, a containers

were equilibrated in a horizontal shaker for periods ranging from 1-15 hrs. At the end of the equilibrium period, the solutions were analyzed for the hexavalent or as described earlier. The concentration of Cr(VI) remaining in the equilibrated solutions was plotted as a function of

equilibration period for CSC as shown above. Examination of these figures show that concentration of Cr(VI) understudy falls rapidly with in a period of 3 hrs and the sorption was virtually completed with in 5-6 hrs in the case CSC.

In order to get overall rate constant for the concentration of Cr(VI) is used, the values of u(t) described by equation (6) were calculated, form the above figures for each concentration of Cr(VI), the equilibrium concentration of Xe were determined from the flat portions of the curves. The concentration of chromium (VI) at any given time(x) prior to attainment of equilibrium was also established from the plot. The u (t) values were then obtained by dividing the difference between the initial chromium (VI) concentration and the concentration at any given time(X) by the

difference between the initial concentration and the equilibrium concentration of Cr(VI)(Xe) found out from the graph. The u(t) values were calculated for chromium (VI) for CSC and the values are presented in Table2

The log of [1-u(t))] values were plotted against the corresponding time for chromium (VI) figures 17 to 20 represent a curves obtained for chromium (VI) with cotton seed carbon (CSC). The straight-time nature of these curves for all Cr (VI) concentrations, for CSC indicated that sorption could be approximated to first order reversible kinetics. The straight portions of the curve used for obtaining the slope values which gives the overall rate constant K of the process, the forward k_1 and backward k_2, rate constants were calculated using equation (6). These data can be seen in Table 2.

TABLE – 2
Rate constant for the removal of Cr (VI) by CSC at pH 1.0 & 2.0

S.No	pH	Initial concentration of Cr(VI) solution (mg/lit)	Overall rate constant K(hour)-1	Forward rate constant K1(hour)-1	Backward rate constant k2(hour)-1
1	1.0	10	0.0554	0.0461	0.0093
2	1.0	7	0.0477	0.0272	0.0205
3	1.0	5	0.0480	0.0096	0.0384
4	1.0	3	0.0500	0.00833	0.0417

S.No	pH	Initial concentration of Cr(VI) solution (mg/lit)	Overall rate constant K(hour)-1	Forward rate constant K1(hour)-1	Backward rate constant k2(hour)-1
1	2.0	10	0.0545	0.0213	0.0332
2	2.0	7	0.0771	0.0431	0.034
3	2.0	5	0.0900	0.0308	0.0592
4	2.0	3	0.0800	0.0157	0.0643

It could be seen from the Table that at pH 1.0, the overall rate constants remained constant whereas at pH2.0, as the concentration of Cr (VI) decreases the rate constant increases Moreover due to extensive reduction that occurs at pH1.0,the forward rate constant is higher than the backward rate constant. However at pH 2.0, the backward rate constant is more than the forward rate constant suggesting that the adsorption mechanism operates predominantly.

CONCLUSION

The results have clearly demonstrated that cotton seed carbon could be employed successfully for the removal of hexavalent chromium. The carbon has moderate hardness and surface area so that it can be applied for wastewater treatment containing heavy metals such as Cr (VI).

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