

A Simple Method for Elimination of Wastewater Containing Cr (VI) ion using Adsorption on Low Cost Adsorbent

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Abstract – The use of low-cost adsorbents has been investigated as a replacement for costly adsorbents and methods of removing Cr (VI) ions from aqueous solution. The purpose of this review article is to provide the scattered available information on various aspects of utilization of low-cost adsorbents derived from agricultural waste, industrial by-products and waste material or natural material. To highlight their technical applicability, selected information on initial chromium concentration, pH level, dose required, adsorption capacity, temperature, thermodynamic data, adsorption isotherm, adsorption kinetics is presented. In general, technical applicability and cost-effectiveness are the key factors in the selection of the most suitable adsorbent to treat aqueous solution contain nickel ions.

Keywords – Adsorption, Low-Cost Material, Cr ((VI), Aqueous Solution.

I. INTRODUCTION

Water is an essential element for the ecosystem and has been termed as the “Elixir of life”. It is one of the most important commodities which human being has exploited than any other resource for the substance of their life. Water is a transparent fluid which forms the world’s streams, lakes, oceans and rain, and is the major constituent of the fluids of living things. Water is also required for economic growth and development. In spite of this, safe drinking water is not available in some parts of the world. Actually, only 1 % of the world’s water is usable to us. About 97 % is salty seawater and 2 % is frozen in glaciers and polar ice caps. Thus that 1 % of the world’s water supply is a precious commodity necessary for our survival. Water is the dispersion medium for all biochemical reactions of the living process and takes part in many of these reactions. It is necessary for the digestion of food, the elimination of toxins and waste materials, the circulation of body fluids like blood and lymph, and to help regulate body temperature. Water provides a moist environment for all body tissues and cushions joints and protects tissues and organs.

The amount of heavy metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Se, V, and Zn) produced from metal industry, agricultural activity, and waste disposal has increased dramatically. Chromium is a non-biodegradable toxic heavy metal ion present in wastewater. The main source of Chromium pollution in the water derives from industrial production processes such as galvanization, smelting, mining, batteries manufacturing and metal finishing. Chromium can cause serious health and ecological problems when released into the environment

Experimental

50 g of dried cottonseed cake treated with 200 g of sulphuric acid and then kept in an air oven maintained at 140-160⁰c for a period of 24 hours. The product was washed with water to remove sulphuric acid and dried at 110⁰c. After the acid process was completed the material was thermally activated using muffle furnace

maintained at 800⁰ c . This carbon taken in the size range (20-50 mesh) CSCC 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 (CSCC)

S. No.	Description	Results
1	Moisture content, %	12.54
2	Bulk density, g/cc	0.59
3	Matter soluble in water, %	2.58
4	Decolorizing power, mg/g	0.19
5	Matter soluble in acid, %	5.63
6	Ash, %	8.04
7	Surface area sq.m/g	532.4
8	Phenol number	18
9	Ion exchange capacity milli equivalent / g	0.299
10	Iron contents, %	1.49

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- diphenyl 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.

II. 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 cake 1carbonized with sulphuric acid after thermal activation at 800⁰c was taken for experimental purposes. This carbon taken in the size range (20-50mesh) (CSCC) 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 CSCC. However it was decided to maintain equilibration time of 3 hours in all subsequent experiments.

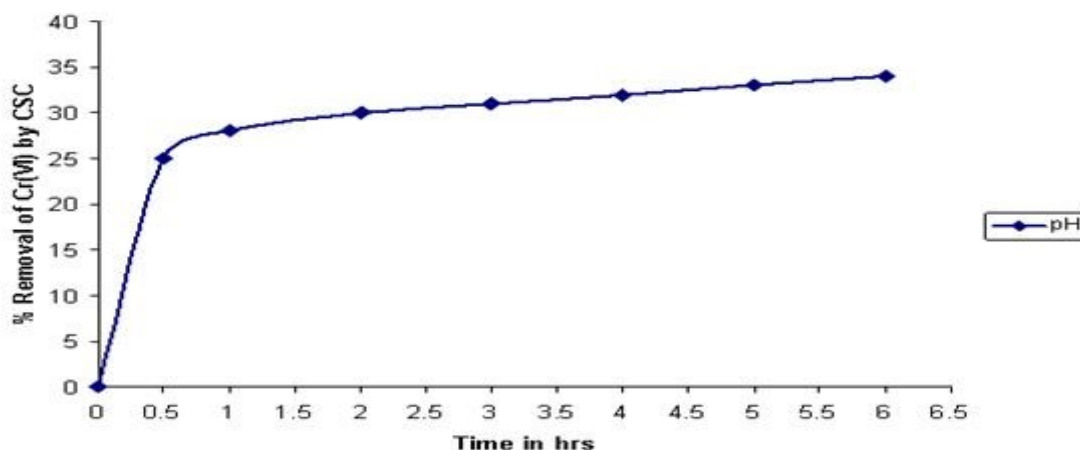


Fig. 1. Effect of Time for the Removal of Cr (VI) of Concentration 10mg/L-Carbon Dose 100mg/100mL; pH: 5.0.

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 CSCC. The removal of chromium (VI) falls gradually over the pH range 3 to 5 and practically remains constant from pH 5.0 to 9.0.

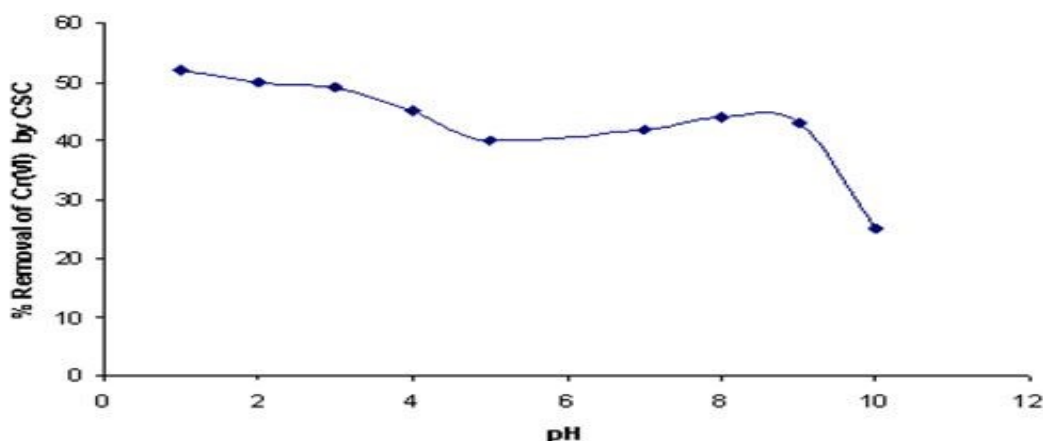


Fig. 2. Effect of pH on Adsorption of Cr (VI) of Concentration 10mg /L-Time: 3hrs: Carbon Dose 100mg/100mL; pH: 5.0-9.0.

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 range 1.0-7.0. 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.

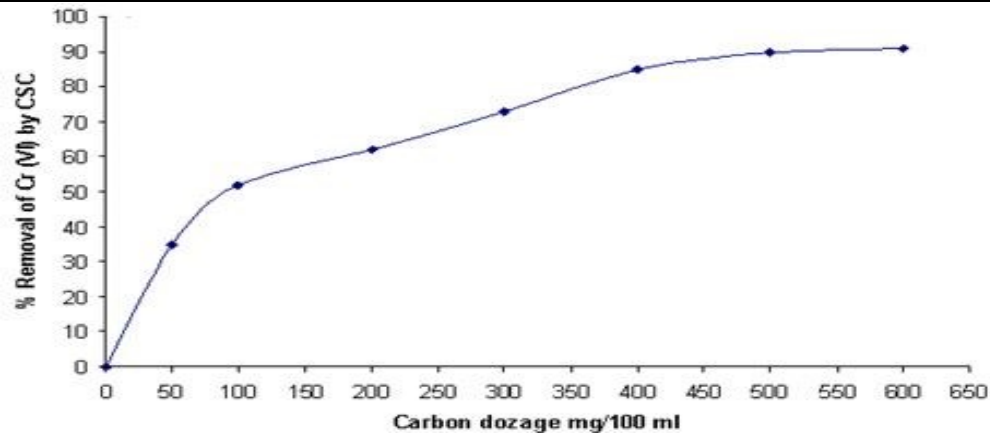


Fig. 3. Effect of Carbon Dosage on Adsorption of Cr (VI) of Concentration Time 3Hrs; pH : 1.

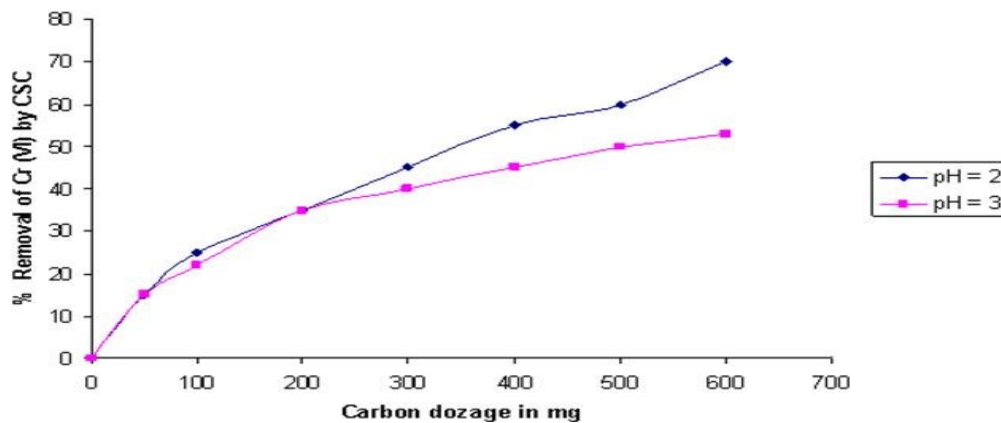


Fig. 4. Effect of Carbon Dosage on Adsorption of Cr(VI) of Concentration 10mg/L 10mg/L-time 3Hrs ; pH :2 & pH: 3.

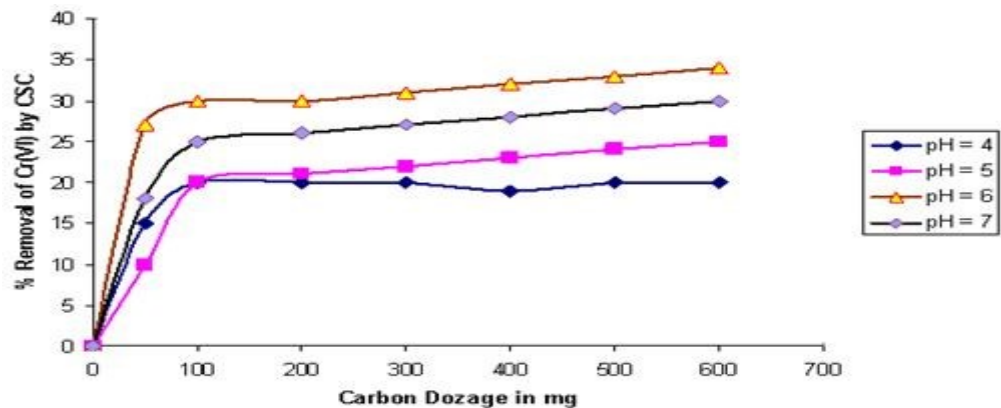


Fig. 5. Effect of Carbon Dosage on Adsorption of Cr (VI) Of Concentration 10mg/L- Time 3Hrs; pH : 4 to 7

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 29%. 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.

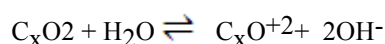
Mechanism of Cr (VI) Removal

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>4.5⁹. In other words, Chromate ions are the major species available at high pH condition (>8.0).

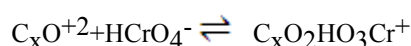
In the case of trivalent chromium, positively charged hydrated species occurs in the pH ranges 0-2.5. Over the pH ranges 4.0-6.0 the positive charge on the hydrated species decreases and eventually hydrated chromium species appears at pH conditions greater than 6.0.

According to Shilov, Shatunovska, Chmutov¹⁰ and Frumkin¹¹ groupings such as C_XO or C_XO₂ 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.



Based upon the above reaction, Huang and Wu¹⁴ 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,



An overall reaction scheme was obtained by combining equations (1) and (2).



Freundlich Adsorption Isotherm

The Freundlich adsorption equation is the widely used mathematical description of adsorption in aqueous systems. The equation is expressed as¹⁵,

$$X/m = K.C_e^{1/n} \quad \dots\dots\dots 1$$

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,

$$\text{Log } x/m = \text{log } K + 1/n \text{ log } C_e \quad \dots\dots\dots 2$$

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),

$$\text{Log } [(Co-Ce)/m] = \text{log } K + 1/n \text{ log } C_e \quad \dots\dots\dots 3$$

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 (CSCC) experiments were conducted with different initial concentrations of Cr (VI) over the 10-60 mg/l 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 an elevated level than the adsorption isotherm drawn for tap 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.

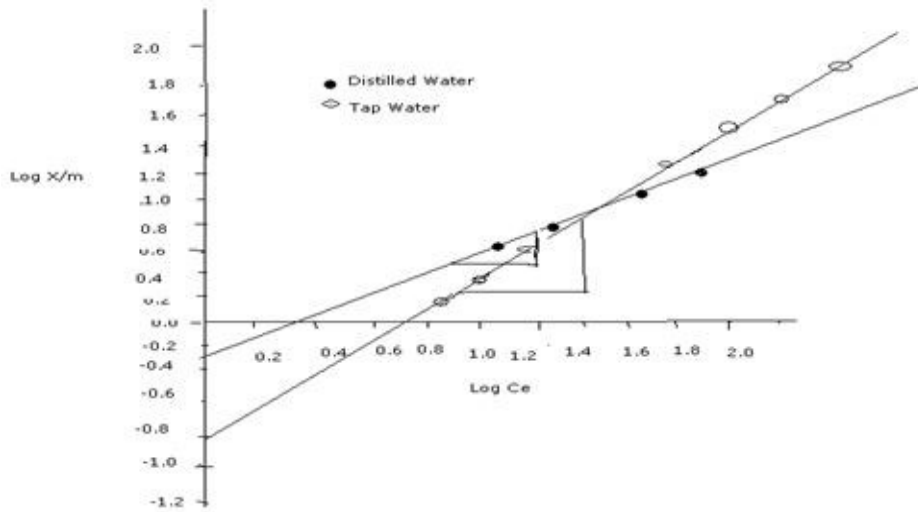


Fig. 6. Freundlich Adsorption Isotherm for the Adsorption of Cr (VI) ; Time: 10Hrs: pH: 1.

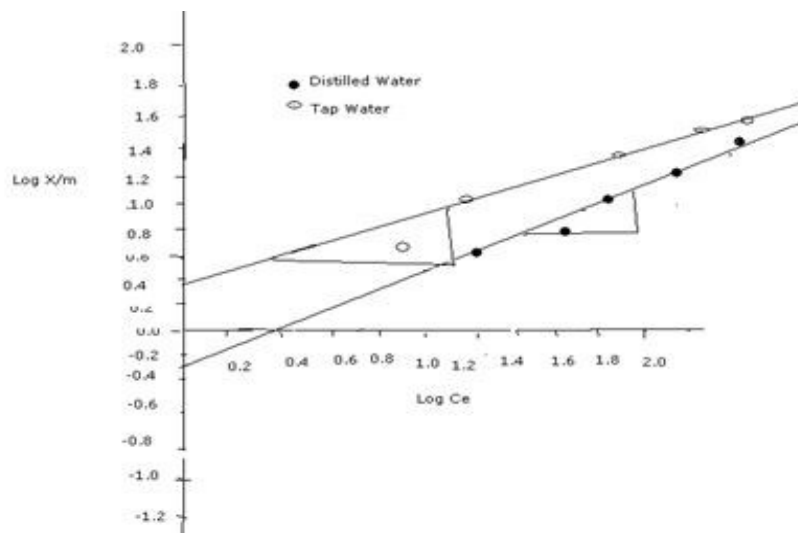


Fig. 7. Freundlich Adsorption Isotherm for the Adsorption of Cr (VI) ; Time: 10Hrs: pH: 2.

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 (CSCC) from the slope of the straight-line curve.

The Freundlich equations in the case both distilled water and tap 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.

IV. 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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 - (ii) "Adsorptive removal of lead (II) from an aqueous solution by chemically modified cottonseed cake" International Journal of Research on Chemical Intermediates, Vol.41, No.7, 2015.
 - (iii) "Studies on the removal of Ni (II) from aqueous solution by activated Carbon developed from Cottonseed Cake Activated with sulphuric Acid International Journal of Chemical Science, Vol.13,No.2,Page No. 817-829,2015
 - (iv) "Studies on the removal of Cr (VI) from aqueous solution by activated carbon developed from Cottonseed activated with sulphuric acid" International Journal of Chem Tech Research, Vol. 8. No. 2, 2015.
 - (v) "Synthesis, Characterization & Antimicrobial Studies of Nickel (II) Chelates of some Salicylidene Schiff bases" International Journal of Chem Tech Research, Vol. 8.No. 2, 2015.
 - (vi) "Adsorption Of Heavy Metals: A Review" European Journal Of Pharmaceutical And Medical Research, Vol.4, No. 11, pp. 174-177, 2017.
 - (vii) "Adsorption of Cu(II) ion from aqueous solution using acid treated sago waste as an adsorbent" European Journal Of Pharmaceutical And Medical Research, Vol.4, No.11, pp. 296-301, 2017.