Decontamination of Chromium Containing Ground Water by Adsorption Using Chemically Modified Activated Carbon Fabric

J. R. Mudakavi, K. Puttanna

Abstract—Chromium in the environment is considered as one of the most toxic elements probably next only to mercury and arsenic. It is acutely toxic, mutagenic and carcinogenic in the environment. Chromium contamination of soil and underground water due to industrial activities is a very serious problem in several parts of India covering Karnataka, Tamil Nadu, Andhra Pradesh etc. Functionally modified Activated Carbon Fabrics (ACF) offer targeted chromium removal from drinking water and industrial effluents. Activated carbon fabric is a light weight adsorbing material with high surface area and low resistance to fluid flow. We have investigated surface modification of ACF using various acids in the laboratory through batch as well as through continuous flow column experiments with a view to develop the optimum conditions for chromium removal. Among the various acids investigated, phosphoric acid modified ACF gave best results with a removal efficiency of 95% under optimum conditions. Optimum pH was around 2 – 4 with 2 hours contact time. Continuous column experiments with an effective bed contact time (EBCT) of 5 minutes indicated that breakthrough occurred after 300 bed volumes. Adsorption data followed a Freundlich isotherm pattern. Nickel adsorbs preferentially and sulphate reduces chromium adsorption by 50%. The ACF could be regenerated up to 52.3% using 3 M NaOH under optimal conditions. The process is simple, economical, energy efficient and applicable to industrial effluents and drinking water.

Keywords—Activated carbon fabric, adsorption, drinking water, hexavalent chromium.

I. INTRODUCTION

ACTIVATED carbon fiber (ACF) is a flexible form of activated carbon [1]. It is highly porous but mechanically weaker than granular activated carbon. ACF exhibits 40% nanopores in addition to numerous micropores and mesopores which makes it an ideal material for adsorption of organic and inorganic pollutants. Due to its fibrous nature fast adsorption takes place in both gas and liquid phases. Toxic elements and organic compounds exhibit electrostatic affinities towards carbon atoms due to Van der Wall's forces.

Typically, weak bonding between the adsorbed molecules facilitates easy removal of adsorbed molecules by heating. Pretreatment of activated carbon imparts specific properties to ACF. Surface complexes with hetero atoms such as O, N, S, P etc. exert profound influences on the surface properties of ACF such as acidity, cation and anion exchange capacities,

J. R. Mudakavi and K. Puttana are with the Dept. of Chemical Engineering, Indian Institute of Science, Bangalore, 560012, India (phone: +91-80-22933107, e-mail: jrm@chemeng.iisc.ernet.in, k.puttanna@gmail.com).

affinities, wettability, porosity etc.

Activated carbon fabric is manufactured by heating viscose under reducing conditions [2]. ACF has also been prepared using phenol, naphthalene or other organic compounds impregnated on polypropylene felt cloth [3]. ACF has also been prepared from Rayon cloth in liquefied petroleum gas (LPG) atmosphere using a specially designed furnace whose temperature varied from 300 to 1000° C in a uniform temperature gradient. Compared to granular activated carbon (GAC) and activated carbon powder (ACP), ACF offers high surface area, low resistance to flow of liquids and gases and possibility of thermal desorption of adsorbed gases. Our preliminary experiments showed that ACF is a prime candidate for the removal of toxic hexavalent chromium from contaminated water [4].

Chromium exists in nature mainly in +3 and +6 oxidation states. It is a micronutrient in trivalent state for animals but highly toxic in hexavalent state [5]. Chromium compounds are widely used in electroplating industries. Some of the other uses of chromium include plastic coatings, corrosion resisting coatings, leather tanning and finishing, pigments, wood preservation and as an alloying element in stainless steel. Chromium occurs in wastewaters resulting from these operations in both trivalent and hexavalent forms. The latter is carcinogenic [5].

The use of activated carbon fabric came into focus in the beginning of the First World War. The advent of gas warfare necessitated the development of protective respiratory devices for the use of personnel engaged in war. A variety of carbon containing raw materials is used for the preparation of activated carbon. Common starting materials for activated carbon include lignite, peat, wood, saw dust, nut shells, rice husk, peat, refinery residue or coal etc. These materials are generally mixed with an alkali metal sulfate, carbonate or phosphate or zinc chloride and then calcined at 500-900ºC.

The calcined mass is washed, filtered and dried [6]. The raw materials to make activated carbon must meet several requirements such as abundant availability, high carbon content, easy activation, low degradation during storage, and low cost [7]. Byproducts of agro industries such as coconut shells, almond shells, hazelnut shells, cherry stones, eucalyptus, apricot shells, nuts, grape seeds, olive and peach stones, sugar cane bagasse, oil palm trunks etc., meet these requirements as they are abundantly available and inexpensive [8].

Activated carbon derived from various sources is the most

investigated adsorbent in adsorption of chromium [9]. Pore size distribution and surface area, outer surface qualities and chemical composition etc., strongly affect the capacity, selectivity, regenerability, the kinetics of adsorption and compatibility. Activated carbon fabric adsorption seems to be an attractive choice for chromium removal owing to its exceptionally high surface area (1500-2500 m^2 g^{-1}), well developed internal microporous structure and the presence of a wide spectrum of surface functional groups like hydroxyl, carboxyl etc. For these reasons, activated carbon adsorption has been extensively used for the treatment of chromium containing wastewaters [10].

Based on its size and shape, activated carbon is classified into four types: Powder-activated carbon (PAC), granular-activated carbon (GAC), activated carbon fiber (ACF), and activated carbon cloth (ACC). Due to the different sources of raw materials and the chemical activation process, and the physicochemical characteristics of each type of activated carbon differ widely and hence suitable for specific application. ACF exhibits inherent advantages and disadvantages in wastewater treatment [11].

In the present study ACF manufactured with 5 percent phosphoric acid activation has been studied as a possible adsorbent for removing chromium from synthetic as well as underground contaminated waters. The main object was to study the efficiency of the material in batch and continuous processes. This paper presents our investigations on the use of activated carbon fabric (ACF) for removing hexavalent chromium from contaminated water. The role of the initial concentration, adsorbent dosage and effect of other concomitant ions has been investigated in this study.

II. MATERIALS AND METHODS

All the chemicals used in this study were of analytical grade. A double beam diode array spectrophotometer (350 – 800 nm) Biochrome Libra S6, Thermo M Series Flame atomic absorption spectrometer and Micropro Grad Mate-CD pH meter, provided with a combined glass electrode were used in this work.

A. Preparation of Solutions

1. Stock Chromium Solution (100 ppm): 0.0283 g of potassium dichromate was dissolved in deionised water and made up to 100 ml
2. Standard chromium Solution (5 ppm): 5 ml of the stock fluoride solution was diluted to 100 ml with deionised water
3. Diphenylcarbazide (DPC) Solution: 0.1250 g of diphenylcarbazide was dissolved in acetone and diluted to 50 ml with acetone
4. Hydrochloric Acid (1N): 8.5 ml of conc. hydrochloric acid was diluted to 100 ml with deionised water
5. Copper Sulphate (100 ppm Cu2+)
6. Potassium Persulphate 10 mM

B. Preparation of Calibration Curve

Calibration curve for 1 to 5 ppm chromium was prepared using flame atomic absorption per the standard procedure.

For spectrophotometry aliquots of standard chromium solution covering 0 to 2.5 ppm were treated with 2 ml hydrochloric acid and 0.5 ml diphenylcarbazide solution and diluted to 10 ml. The absorbances of the solutions were measured after 10 minutes of mixing at 545 nm against the blank. From this data calibration curve for hexavalent chromium was prepared [12].

C. Determination of Total Chromium

For the determination of total chromium in a solution containing both Cr^{6+} and Cr^{3+}, an aliquot of the sample was oxidized by heating with 20 μg of Cu^{2+} and 1 ml of 10 mM potassium persulphate for 1 h. The solution was cooled and treated with DPC to develop color which was measured as before and referred to the same calibration curve.

Phosphoric acid activated ACF sample was obtained from M/S Environcare Products, Greater Noida, India. The sample had a moisture content of 0.88 %, pH of 3.47, 30 % volatile content and an ash content of 3.4 %. Surface area was determined by BET method using an ASAP 2020 instrument and V3.03 H version software. To remove all the gaseous molecules adsorbed on ACF, the sample was heated to 900° C for 1 h followed by heating at 250° C for 4 h under vacuum. Adsorption investigations were carried out on pretreated ACF by exposing it to a jet of nitrogen molecules.

Initially investigations were carried out with synthetic chromium solution. Chromium contaminated bore well samples were obtained from the factory premises of an electroplating industry located in Yelahanka, Bangalore. This sample was analyzed in our laboratory by both DPC method and flame atomic absorption spectrometry. The sample was found to contain 162 ppm of hexavalent chromium. This sample was diluted to 50 ppm and used in all subsequent application studies.

D. Design and Construction of the Column for Continuous Adsorption Studies

A 50 ml burette was taken and cleaned with acetone. It was dried and filled with cotton up to 4 cm followed by glass beads up to 4 cm height from the bottom. Different weights of ACF were weighed and cut into small pieces. These ACF were placed in the column. The ACF was topped with 4 cm glass beads followed by another cotton plug. At the top of the column a funnel was attached and made leak proof. This column was clamped to a stand. DI water was filled in the burette and left overnight. Next day, by adjusting the stop cock of the burette, the desired flow rates were obtained. In this way, we prepared two columns containing 5 and 10 g of ACF.

III. RESULTS AND DISCUSSION

Typical properties of ACF are presented in Table I.

A. Calibration Curve

The calibration curve for chromium is presented in Fig.1. The curve was linear up to 2 ppm chromium.

TABLE I
PROPERTIES OF ACF

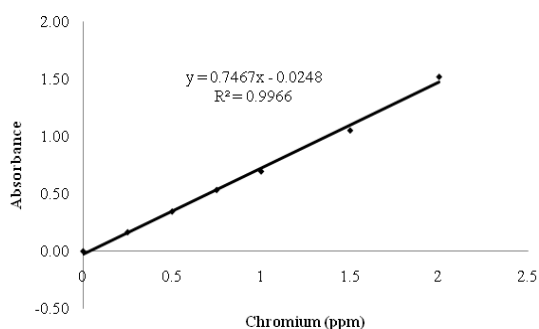| Properties of ACF	Units
Surface area (m^2/g) BET	1754
Pore Volume (cc/g)	0.7 – 0.9
Effective Pore Size (A°)	7-9
Thickness (mm)	0.2 – 0.8
Specific gravity	0.2 – 0.7
Decomposition Temperature (C°)	>500
Texture	Woven
Iodine number	2551.4

Fig. 1 Calibration curve for chromium by DPC method (545 nm)

B. Surface Modification of ACF

0.2 g ACF was weighed into a 250 ml conical flask and 100 ml of 5 % orthophosphoric acid was added. The flask was stirred for 1 h. at 160 rpm in a rotary shaker. The treated ACF was washed with distilled water and finally dried in an oven at 100° C. This was followed by heating in a muffle furnace for 2 hours at 400° C. Similarly, ACF was treated with sulphuric, hydrochloric and nitric acids. These were tested for chromium adsorption. Preliminary experiments suggested that orthophosphoric acid activated ACF was suitable for adsorption of chromium compared to other activation methods such as steam, ZnCl$_2$, CuCl$_2$, hydrochloric and nitric acid activated ACF (unpublished results). Therefore all further studies were carried out with orthophosphoric acid activated ACF.

C. Batch Adsorption Studies

ACF (0.01- 0.2 g) was weighed and treated with 200 ml of 5 ppm chromium solution. The solution was stirred for 1 hour with a magnetic stirrer. The pH of the solution was measured before and after stirring and the filtrate was analyzed for chromium content by diphenylcarbazide method. The experimental parameters used for batch studies are shown in Table II.

1. Effect of pH on the Adsorption of Chromium

pH is an important factor affecting the adsorption process. Normally chromium is present in the effluent as dichromate (Cr$_2$O$_7^{2-}$) or chromate (CrO$_4^-$) ions.

Dichromate and chromate ions can be adsorbed on the carbon matrix by active hydrogen, hydroxyl and phosphatic sites. The effect of initial pH on adsorption of chromium was studied in the range 1-10. The results have been presented in Fig. 2.

TABLE II
PARAMETERS USED IN BATCH STUDIES

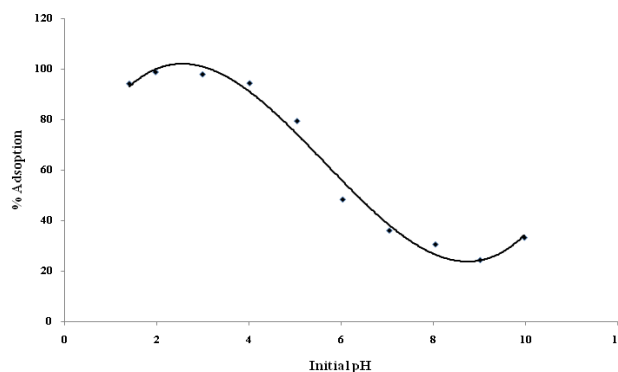| Weight of ACF (g)	Flow rate (ml/min)	Input Cr(VI) Conc (ppm)
10.00	4.16	5.0
5.00	13.90	5.0
5.00	8.30	5.0
5.00	2.00	5.0

Fig. 2 Effect of initial pH on adsorption of chromium on ACF

It is evident from Fig. 2 that maximum adsorption occurs between pH 2-3. Hence all subsequent studies were carried out at pH 2. Mohan *et al.* have obtained similar results using low cost activated carbons derived from agricultural wastes [9].

2. Effect of Weight of ACF on Adsorption of Chromium

A plot of the weight of ACF versus adsorption of chromium is shown in Fig. 3. It is clear from the figure that 0.2 g of ACF is sufficient to remove all the chromium ions from 200 ml of 5 ppm chromium solution. Therefore, in all further studies 0.2 g ACF was used to study the effect of stirring time, temperature and stirring speed on adsorption.

3. Effect of Contact Time on Chromium Adsorption

Contact time of chromium solution at pH 2 with ACF was varied from 15-120 min. At the end of the reaction, the pH of the filtrates was recorded once again. The above experiment was repeated at pH 5.00. The results are presented in Fig. 4.

It is evident from Fig. 4 that the concentration of chromium falls asymptotically with time whereas the percent adsorption of chromium increased in a similar manner. At pH 2 up to 97.8 % chromium was adsorbed on ACF whereas only 83 % was adsorbed at pH 5. This result indicates that for better removal of chromium from contaminated water requires higher contact time. If a column is employed to remove chromium the flow rate should be as low as possible for a given diameter of column cross section.
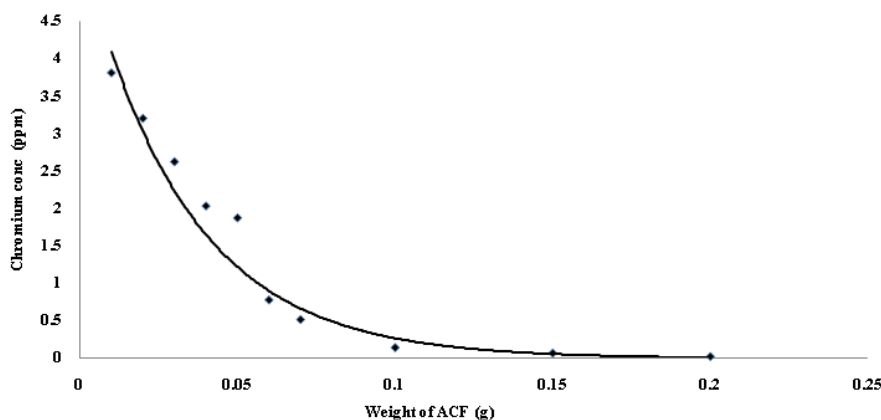
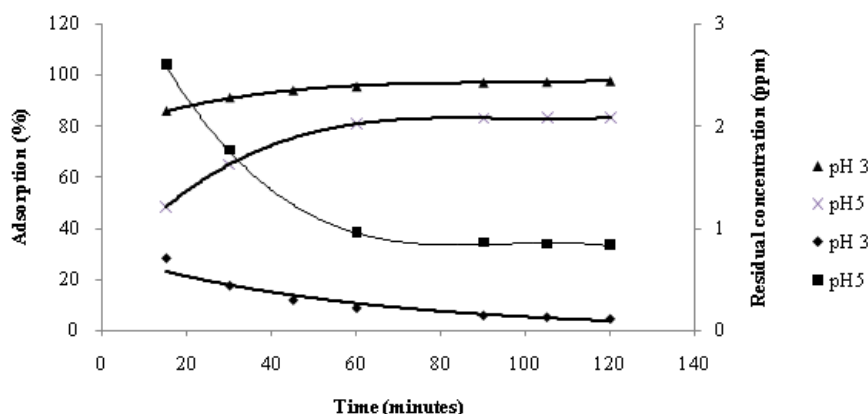Fig. 3 Effect of weight of ACF on residual chromium concentration

Fig. 4 Effect of contact time on chromium adsorption

4. Effect of Preheating ACF

The effect of preheating of ACF on adsorption of chromium is presented in Table III.

TABLE III
EFFECT OF PREHEATING ACF ON THE ADSORPTION OF CHROMIUM

Weight of ACF (g)	Pre-heating	pH of filtered solution	Filtrate Conc. (ppm)	Total Cr Adsorbed (µg)	Percent Cr adsorbed
0.20	Yes	2.97	0.03	994	99.4
0.15	Yes	3.00	0.08	984	98.4
0.05	Yes	3.03	2.85	430	43.0
0.20	No	2.75	0.02	996	99.6
0.15	No	2.81	0.06	988	98.8
0.05	No	3.08	1.87	626	62.6

It can be easily seen from Table III that preheating the ACF did not have significant effect on the adsorption of chromium. Whereas preheating serves to remove gases that might have been adsorbed on ACF but in our work this has no bearing on the adsorption of chromium. Still it is advisable to keep the ACF protected from exposure to air before using.

5. Effect of Stirring Speed

The stirring speed was varied between 100-260 rpm. The results are presented in Table IV. The optimum speed of stirring was 260 rpm. Therefore, in all further work stirring was done at 260 rpm.

TABLE IV
EFFECT OF STIRRING SPEED ON CHROMIUM ADSORPTION

ACF (g)	RPM	Filtrate conc. (ppm)	Total Cr Adsorbed (µg)	Percent Adsorbed	Adsorption mg/g
0.2	100	1.494	701.2	70.1	3.5
0.2	150	1.017	796.6	79.7	4.0
0.2	200	0.545	891	89.1	4.5
0.2	230	0.159	968.2	96.8	4.8
0.2	260	0.080	984	98.4	4.9

6. Effect of Initial Concentration of Chromium

The effect of initial concentration of chromium was studied next in the range 2-10 ppm. The data is presented in TABLE V, from which it is evident that at higher initial concentrations of chromium the concentration in the filtrate increased. Hence under the experimental conditions 98.4 % adsorption of chromium occurs at 5 ppm above which the efficiency decreased to 60.3 % at 10 ppm.

7. Adsorption Isotherms

The adsorption data fitted well into Freundlich isotherm. The linearized form of the isotherm is presented in Fig. 5. Maximum adsorption capacity of chromium on ACF was

found to be 13.71 mg / g. Mohan *et al.* reported a somewhat higher value of 22.29 [9]. However, their results are based only on batch adsorption.

TABLE V
EFFECT OF INITIAL CONCENTRATION OF CHROMIUM ON ADSORPTION

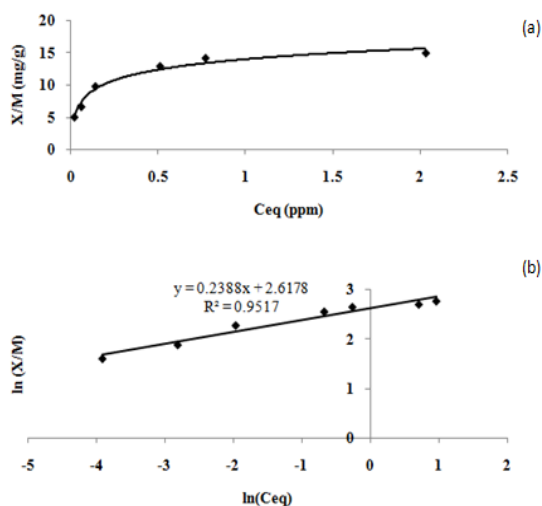| Initial conc of Cr solution (ppm)	Concentration of filtrate (ppm)	Total Cr Adsorbed (µg)	Percent Adsorption
2	0.02	996	99.7
4	0.04	992	99.2
5	0.08	984	98.4
6	0.22	956	95.6
8	0.78	844	84.6
10	2.01	598	60.3

Fig. 5 (a) Normal and (b) linearized Freundlich plot for adsorption of Cr^{6+} on ACF (n = 4.188 and K = 13.706)

8. Effect of Concomitant Ions

In the present investigation, all experiments were carried out using pure dichromate solution. However, in industrial effluents, several other ions are also expected to be present which can compete with chromium for adsorption sites. Therefore, the effect of common interfering ions such as chloride, sulphate, iron, cobalt and nickel on the adsorption of chromium was studied. Experiments were conducted with 5 ppm chromium and 5 ppm each of concomitant ions. The data presented in Table VI shows that nickel and sulphate interfere strongly.

TABLE VI
EFFECT OF CONCOMITANT IONS ON THE ADSORPTION OF CHROMIUM

Concomitant (5 ppm)	Cr conc in filtrate (ppm)	Total Cr Adsorbed (µg)	Percent Chromium Adsorbed
Iron (Fe^{3+})	0.011	997.8	99.8
Cobalt (Co^{2+})	0.534	893.2	89.3
Nickel (Ni^{2+})	4.110	178	17.6
Chloride (Cl^-)	0.576	884.8	88.6
Sulphate (SO_4^{2-})	2.351	529.8	53.0

Consequently, chromium adsorption decreases to 17.6 % and 53.0 %, respectively. Chloride and cobalt exhibited somewhat weaker interference decreasing the adsorption capacity to 89.3 % and 88.6 %. Iron did not interfere significantly.

D. Desorption Studies

Desorption of chromium from ACF permits the recovery of chromium as well as recycling of ACF. We have investigated the desorption of chromium from spent ACF. In these experiments 0.2 g of ACF was shaken with 500 ml of 5 ppm chromium solution. The chromium adsorbed ACF was washed thoroughly with distilled water and dried in an oven at 100°C.

TABLE VII
DESORPTION OF CHROMIUM

Concentration of NaOH (M)	Concentration of filtrate (ppm)	Chromium Desorbed (mg)	Percent Desorption
0.1	6.53	0.065	6.8
0.2	8.47	0.085	8.9
0.3	9.77	0.098	10.2
0.4	12.89	0.129	13.4
0.5	35.06	0.351	36.5
1.0	37.22	0.370	38.5
2.0	42.39	0.420	43.8
3.0	51.82	0.520	54.2

ACF so prepared (ACF-Cr) had 960 µg Cr^{6+} adsorbed on it which was used for desorption studies. Desorption was studied by shaking 0.2 g of ACF – Cr with 10 ml of 0.1-3.0 M NaOH. The suspension was filtered and the filtrate was analyzed for total chromium by a modified diphenylcarbazide method after neutralization with 2N hydrochloric acid.

The results from TABLE VII show that desorption increases with increasing concentration of NaOH. Hydrochloric, sulphuric, nitric and orthophosphoric acids at 5-50 % strength were also tried but were found to be ineffective.

E. Continuous Adsorption Studies

ACF filled column was used for continuous adsorption studies. The flow rate was adjusted between 4.16-13.9 ml/min. The column was washed with distilled water initially and then 5 ppm solution of hexavalent chromium was fed and the eluent was collected. 5 ml aliquots of the eluent was collected after every 250 ml and analyzed for chromium content. The experiment was continued till the ACF column was saturated with chromium as indicated by no further change in the eluent chromium concentration.

Chromium adsorbed on ACF was calculated. Parameters such as quantity of ACF, flow rate and input chromium concentration on column adsorption were studied as shown in Table VIII.
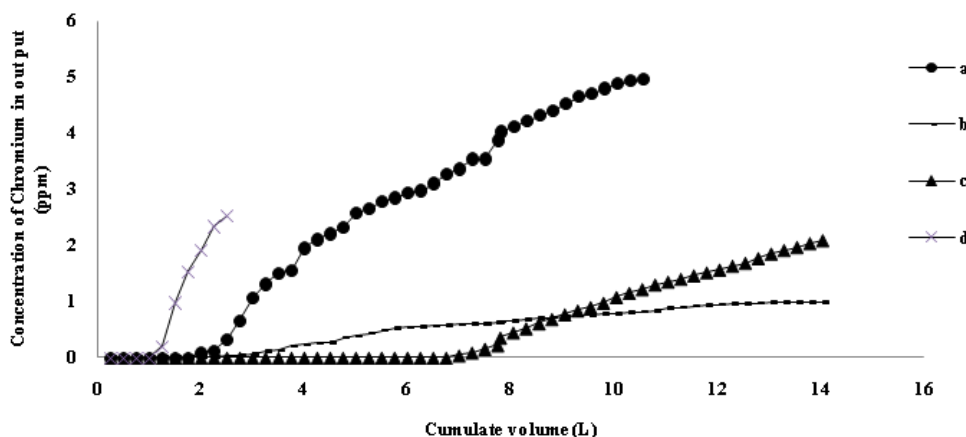
Fig. 6. Continuous process studies at flow rates of 13.9 (a), 8.3 (b), 4.16 (c) and 4.2 ml/min (d): 21 cm^3 bed volume. (a)-(c) for 5 ppm chromium and (d) is for industrial water adjusted to 50 ppm

TABLE VIII
COMBINATION OF EXPERIMENTAL VARIABLES USED IN THE STUDY

Weight of ACF (g)	Flow rate (ml/ min)	Input Cr(VI) conc. (ppm)
10.00	4.16	5.0
5.00	13.90	5.0
5.00	8.30	5.0
5.00	2.00	5.0

The results are presented in Fig. 6. Fig. 6 shows that at 13.9 ml/min flow rate, with 5 ppm Cr (VI), up to 100 bed volume of treated water having < 0.05 ppm chromium could be obtained. This is suitable for drinking. The quantity of effluent that could be treated increased dramatically at lower flow rates. Thus, at 8.3 ml/min flow rate the output up to 1000 times the bed volume did not contain chromium and hence it is safe to drink. Similarly, at 4.2 ml/min flow rate up to 1250 bed volumes of treated water did not contain chromium. Thus it is clear that lower flow rates result in greater volumes of chromium free water.

F. Investigations with Industrial Sample

A contaminated underground water sample obtained from an industry located in Bangalore was found to contain 160 ppm chromium. It was diluted to 50 ppm chromium and adjusted to pH 2. It was fed into a column containing 5 g ACF at a flow rate of 4.2 ml/ min. The aliquots were analyzed for chromium content similar to the procedure described earlier. About 1200 ml of chromium containing water could be decontaminated by using 5 g ACF.

Based on these results, a simple process for the treatment of industrial waste waters has been proposed. A schematic diagram of the process is presented in Fig. 7 which contains an equalizer tank, pH modifier, a filter, adsorption column followed by another pH modifier to adjust the output effluent to pH 7 which would contain < 0.05 ppm chromium.

The design process has been optimized to treat 2000 L/h of underground water containing 50 ppm of chromium. The equipment specifications have been presented in TABLE IX. Under optimum operating conditions, we have established that up to 4,80,000 litres of the effluent can treated at a cost of Rs.

1.50 per liter. A series of columns needs to be employed to facilitate change of saturated columns.
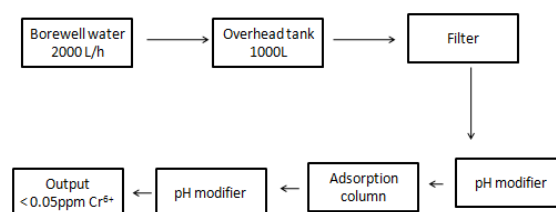

Fig. 7 Schematic diagram of the proposed process for removing fluoride from drinking water

TABLE IX
INPUT DESIGN PARAMETERS OF THE PROPOSED PROCESS

Equipment	Cost (Rs)
2 Holding Tanks 1000 L	10,000*
Pumps, 2, 0.5 HP	20,000
Fitting layout, piping, labour, safety	25,000
pH treatment tanks (concrete with epoxy)	1,00,000
Adsorption Column (1 x 5 m) MS with fittings	2,50,000
Escalation 30%	1,20,000

IV. CONCLUSIONS

The present study proves beyond doubt that orthophosphoric acid activated ACF is an excellent material for chromium adsorption. Optimum parameters affecting the adsorption of chromium on ACF have been investigated and the results are utilized to develop a process for remediation of chromium contaminated underground water. Both batch and continuous column process have the potential to treat the effluents. There are very little interference in the process. The following are the important findings from this study. Only 0.2 g of ACF is sufficient for complete removal of chromium from 200 ml of 5 ppm solution. Optimum adsorption takes place around pH 2-3. For other pH values, adsorption decreases. This necessitates a pre-pH adjustment step and post column treatment of the effluent. Decreasing the flow rate or

increasing the contact time increases the capacity of the column to adsorb chromium. To exploit the residual capacity of ACF to adsorb chromium after break through, several columns in series should be employed. Presence of ions like nickel and sulphate decreases the capacity of ACF to remove chromium. Desorption can be achieved by passing a solution of NaOH.

REFERENCES

[1] Y. S. Young, Park, Y. Heum, C. Rae, "Preparation and properties of activated carbon fabric from acrylic fabric waste" *Carbon*, vol. 38, no. 10, pp.1453-1460, Jan 2000.

[2] T. Kazuo, T. Noriyoshi, M. Hiroshi, K. Kazumi, S. Yuki, H. Hirotaka, Y. Naotaka, S. Hiroyuki Method for Producing Activated Carbon Nonwoven, Patent Abstracts of Japan, Mar 2008 patno:JP2008069492

[3] G. N. Arons, R. N Macnair, "Activated Carbon Fiber and Fabric Achieved by Pyrolysis and Activation of Phenolic Precursors" *Textile Res. J*, vol. 42, no. 1, pp.60-63, Jan. 1972.

[4] D. Mohan; K. P. Singh and V. K. Singh "Removal of hexavalent chromium from aqueous solution using low-cost activated carbons derived from agricultural waste materials and activated carbon fabric cloth.*" Ind. Eng. Chem. Res, vol.* 44, pp1027-1042, 2005.

[5] L. McNeill, J. McLean, M. P. Edwards, "State of the Science of Hexavalent Chromium in Drinking Water" *J. Water Research Foundation* 2012.

[6] B. K. Dutta, B. Chaudhuri, A. Ray, "Photoreduction of hexavalent chromium in aqueous solution in the presence of zinc oxide as semiconductor catalyst" *Chem. Eng. J.* vol.153, no.1, pp86-93, 2012.

[7] F. J. Acevedo-Aguilar, A. E. Espino-Saldaña, I. L. Leon Rodriguez, M. E. Rivera-Cano, M. Avila-Rodriguez, K. Wrobel, K. Wrobel, P. Lappe, M. Ulloa, J. F. Gutiérrez-Corona, "Hexavalent chromium removal in vitro and from industrial wastes, using chromate-resistant strains of filamentous fungi indigenous to contaminated wastes" *Can J Microbiol.*, vol.52, no.9, pp809-815, 2006.

[8] Y. Hayashi, T. Kondo, Q. Zhao, R. Ogawa, Z. Cui, L. B. Feril Jr, H. Teranishi, M. Kasuya, "Signal transduction of p53-independent apoptotic pathway induced by hexavalent chromium in U937 cells" *Toxicology and Applied Pharmacology* Vol. 197, nos. 2, pp 96–106, June 2004.

[9] D. Mohan, C. U. Pittman. Jr. "Activated Carbon and new low cost adsorbents fro remediation of tri- and Cr (VI) from water." *J. Hazard. Mat.*, vol. 137, no. 2, pp 762-811, 2006.

[10] M. Owald, M. Aroua, W. A. W. Daud, S. Baroutian "Removal of chromium from contaminated Water and Wastewater: A Review" *Water Air Soil Pollut.*, pp 59-77, 2009.

[11] S. Babel, T. A. Kurniawan "Low cost adsorbents for heavy metals uptake from contaminated water, a review Cr (VI) removal from aqueous solution" J. *Hazard. Mat.*,vol. 97, nos. 1-3,pp 219 – 243, 2003.

[12] L. S. Clesceri, A. E. Greenberg, A. D. Eaton Ed. Standard Methods for the Examination of Water and Wastewater. 20th Edition 1998 American Public Health Association Washington DC.