

Effect of pH on the removal of hexavalent chromium from aqueous solutions using activated carbon

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Abstract

Hexavalent chromium compounds are being used in a wide variety of commercial processes and unregulated disposal of the chromium containing effluent has led to the contamination of soil, sediment, surface and ground waters. In order to mitigate the chromium pollution of urban environment due to effluents from various industries particularly from tannery and electroplating industries this study was under taken. An attempt is made to explore the viability of a low cost effluent treatment. Activated carbon obtained from coconut shell is the sorbent material used. Coconut shell carbon adsorption capacity for chromium (VI) is systematically examined. Understanding the uptake of chromium by activated carbon is an important step to optimize parameters for designing effluent treatment procedures for chromium removal. The effect of pH on the adsorption of chromium (VI) by activated carbon was studied at pH values of 1 to 7. In this investigation the employability of an abundantly available low cost material namely activated carbon from coconut shell for mitigating chromium (VI) pollution is investigated. Different routes for preparing good porous activated carbon has been identified. The results obtained were analyzed for evaluating the use of carbon from coconut shells for chromium removal from solutions. The chromium removal was effective at a pH of 3 and removal efficiency was more than 95%. Optimum contact time has been found to be 50-60 minutes.

1. Introduction

Industrial activities which produces

hexavalent chromium includes chromate pigments in dyes, paints, inks, and plastics; chromates added as anticorrosive agents to

paints, primers, and other surface coatings and chromic acid electroplated onto metal parts to provide a decorative or protective coating. Hexavalent chromium is also formed when "hot work" such as welding on stainless steel or melting chromium metal etc. is undertaken. Hexavalent chromium compounds are being used in a wide variety of commercial processes and unregulated disposal of the chromium containing effluent has led to the contamination of soil, sediment, surface and ground waters.

Effluents from electroplating and tannery industries are a major source of aquatic pollution in India with high chemical oxygen demand (COD), biological oxygen demand (BOD), and hexavalent chromium. There are a large number of tanneries scattered all over the country but the main areas of their concentration are Tamil Nadu, Uttar Pradesh and West Bengal. Nearly 80% of the tanneries in India are engaged in the chrome tanning processes. Most of them discharge untreated wastewater into the environment. In such aqueous waste, Chromium (VI) is present as either dichromate ($\text{Cr}_2\text{O}_7^{2-}$) in acidic environments or as chromate (CrO_4^{2-}) in alkaline environments.

Reduction and chemical precipitation has traditionally been the most used method. The most often used precipitation processes include hydroxide, sulphide, carbonate and phosphate precipitation techniques. The disadvantage of precipitation technique is the production of sludge. This process suffers from draw backs like incomplete removal, requirement of sizable quantities of treatment chemicals and production of voluminous toxic sludge. It constitutes a solid waste disposal problem. A variety of other treatment technologies were

considered and evaluated. Techniques like ion exchange and adsorption with products obtained from naturally occurring materials^{1,2,3} like activated carbon were considered as better alternatives. The exorbitant cost involved with ion exchange makes it prohibitive for wide application.

In order to mitigate the chromium pollution of urban environment due to effluents from various industries particularly from tannery^{4,5} and electroplating industries this study was under taken. An attempt is made to explore the viability of a low cost effluent treatment. Activated carbon obtained from coconut shell is the sorbent material used^{6,7}. Coconut shell carbon adsorption capacity for chromium (VI) is systematically examined. Understanding the uptake of chromium by activated carbon is an important step to optimize parameters for designing effluent treatment procedures for chromium removal.

Coconut shells are available in plenty in tropical countries. The utilization of this waste material helps in recycling waste and thus keeping the eco system clean. Mitigation measures based on low cost technologies hold promise of wide applicability in developing countries⁸. This methodology can be profitably employed by least developed and developing countries in mitigating pollution due to the heavy metal ion chromium.

Effluents from electroplating industries contain heavy metals in amounts greater than the bearing capacity of the surrounding soil or water bodies. This causes pollution of soil and water sources like wells, tanks, rivers, lakes etc. Hence it is advisable to treat effluents from

electroplating industries before it is let out. In some countries it is mandatory to treat (Hazardous waste management). In this context parameters like pH, turbidity, BOD, COD, amount of heavy metals like chromium, nickel, zinc, copper etc. after treatment has to meet certain criteria^{9,10}. In this scenario the present study plays an important role as it addresses the removal of a heavy metal viz., chromium (VI) which is recognized as a carcinogenic material. Also this study evaluates the employment of a waste material generated from food industry (activated carbon prepared from coconut shells).

2. Materials and Methods

Preparation of activated carbon from coconut shells :

Activated carbon is a solid with predominant amorphous structure and it posses an extraordinary internal surface area and pore volume. The well known adsorptive properties are due to these unique characteristics. These are exploited in liquid and gas phase applications. The size and distribution of pores within the carbon matrix can be tailored by control of process conditions like choice of precursors, activation time, dwell time etc to meet the demands of industry. The requirement of specific applications has resulted in the production of active carbon in the form of powder and granular shaped products. The properties of the products can be tailored to suit diverse applications such as treatment of effluents¹¹, control of gasoline emissions, remediation measures for water pollution, soil pollution etc.

The coconut shells were washed with water to remove sticking and lose matter and were sun dried for 5 days (8-10 hours per day). They were hammer broken to pieces and then converted to a powder using a motor operated mixie. Three temperature routes were followed for preparing active carbon by taking known quantities of powdered coconut shell.

Procedure I :

Samples were pyrolysed in a muffle furnace in the presence of steam flow. A two step procedure was followed. Sample was carbonized at 550°C for 2 hours and then a physical activation method was followed for different periods of time.

Through the inspection hole in the muffle furnace door a glass tube was introduced which was connected to a steam generator. Thus a continuous flow of steam was maintained.

Three temperature routes were selected -

Pyrolysing at 750°C and keeping the sample for 40 minutes at a temperature of 750°C
 Pyrolysing at 750°C and keeping the sample for 100 minute at a temperature of 750°C
 Pyrolysing at 800°C and keeping the sample for 30 minute at a temperature of 800°C
 The samples were coded as 750S40, 750S100 and 800S30.

Procedure II :

Powdered coconut shell was impregnated by soaking with 1:1 Ortho phosphoric acid¹² for 12 hours. The powder was washed well until washings showed a pH of 6-7.

Three temperature routes were selected-
 Pyrolysing at 750°C and keeping the sample
 for 40 minutes at a temperature of 750°C

Pyrolysing at 750°C and keeping the sample
 for 100 minutes at a temperature of 750°C

Pyrolysing at 800°C and keeping the sample
 for 30 minutes at a temperature of 800°C

The samples were coded as 750P40, 750P100
 and 800P30

Procedure III :

Powdered coconut shell was impreg-
 nated by soaking with 15% zinc chloride
 solution for 12 hours¹³. The powder was
 washed well until washings showed absence
 of chloride ions.

Three temperature routes were selected-

Pyrolysing at 750°C and keeping the sample
 for 40 minutes at a temperature of 750°C

Pyrolysing at 750°C and keeping the sample
 for 100 minutes at a temperature of 750°C

Pyrolysing at 800°C and keeping the sample
 for 30 minutes at a temperature of 800°C

The samples were coded as 750Z40, 750Z100
 and 800Z30

The samples obtained from the above
 procedures were fine powdered in a motor
 operated pestle and mortar and sieved to
 remove coarse particles. The samples were
 dried in an oven at 110°C for 4 hours and stored
 in desiccators containing silica gel.

3. Results and Discussion

Effect of pH :

The effect of pH on the adsorption of
 chromium (VI) by activated carbon was
 studied at pH values of 1 to 7. 0.5g of activated
 carbon was suspended in 100 ml of solution
 which contained 80 mg of chromium (VI) per
 liter. Different pH conditions were maintained
 by adding HCl and acetic acid-sodium acetate
 buffer. The adsorption of the chromium was
 determined after an equilibration time of one
 hour at a stirring speed of 200 rpm. The various
 values of pH and corresponding % chromium
 removal are tabulated in table 1.

pH influences the adsorption of Cr
 (VI) ions on the adsorbate as it affects the
 solubility of metal ions and hence the
 electrostatic binding of ions. It is evident that
 at lower pH between 2 and 3 the adsorption is
 maximum (Fig. 1,2 and 3). This could be
 attributed to the high concentration of H⁺ ions
 at lower pH values which neutralizes the
 negatively charged adsorbate Cr₂O₇²⁻ ions.
 The decrease in the adsorption efficiency at
 higher pH can be attributed to increase in the
 concentration of OH⁻ ions which hinder the
 diffusion of Cr (VI) ions.

The process of adsorption of metal
 ions on the adsorbent involves the binding of
 metal ions by electrostatic forces of attraction.
 The surface of the adsorbent carry positive
 charges and hence negatively charged Cr₂O₇²⁻
 ionic species are held by electrostatic forces
 of attraction.

It has been suggested that the

Table 1. Data on pH and % Cr removal for S samples
Carbon Dosage: 0.5 g; Temperature: 26°C; Stirring Speed: 200 rpm

Sl. No.	Sample	pH	Initial concentration of chromium in mg in solution	Final concentration of chromium in mg in solution	% Chromium removal
1	750S40	1	180	65	64
2		2	180	36	80
3		3	180	28	84
4		4	180	48	73
5		5	180	77	57
6		6	180	83	54
7		7	180	97	46
8	750S100	1	180	62	66
9		2	180	33	82
10		3	180	25	86
11		4	180	44	76
12		5	180	74	59
13		6	180	80	56
14		7	180	94	48
15	800S30	1	180	60	67
16		2	180	31	83
17		3	180	22	88
18		4	180	42	77
19		5	180	70	61
20		6	180	77	57
21		7	180	92	49

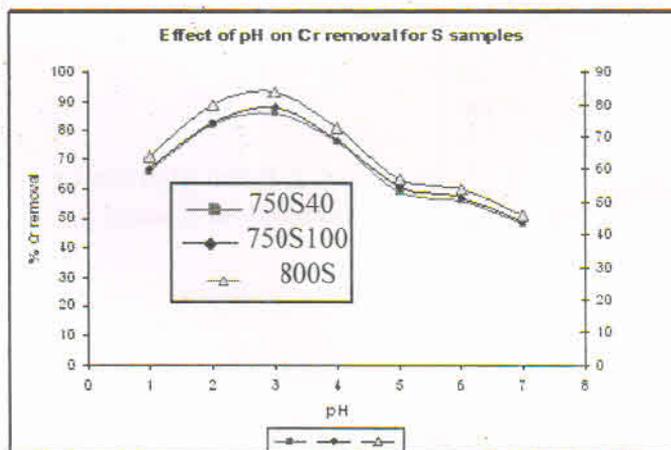


Fig. 1 Effect of pH on Cr removal for S samples

Table 2. Data on pH and % Cr removal for P samples
Carbon Dosage: 0.5 g; Temperature: 26°C; Stirring Speed: 200 rpm

Sl. No.	Sample	pH	Initial concentration of chromium in mg in solution	Final concentration of chromium in mg in solution	% Chromium removal
1	750P40	1	180	61	66
2		2	180	32	82
3		3	180	22	88
4		4	180	45	75
5		5	180	72	60
6		6	180	79	56
7		7	180	95	47
8	750P100	1	180	64	64
9		2	180	36	80
10		3	180	25	86
11		4	180	49	73
12		5	180	74	59
13		6	180	82	54
14		7	180	98	46
15	800P30	1	180	68	62
16		2	180	40	78
17		3	180	29	84
18		4	180	52	71
19		5	180	76	58
20		6	180	86	52
21		7	180	101	44

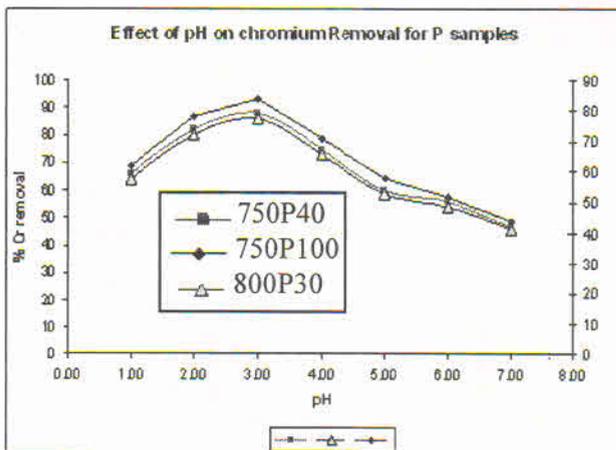


Fig. 2. Effect of pH on Cr removal for P samples.

Table 3. Data on pH and % Cr removal for Z samples
Carbon Dosage: 0.5 g; Temperature: 26°C; Stirring Speed: 200 rpm

Sl. No.	Sample	pH	Initial concentration of chromium in mg in solution	Final concentration of chromium in mg in solution	% Chromium removal
1	750Z40	1	180	54	70
2		2	180	29	84
3		3	180	23	87
4		4	180	23	81
5		5	180	67	63
6		6	180	76	58
7		7	180	85	53
8	750Z100	1	180	48	73
9		2	180	23	87
10		3	180	15	92
11		4	180	31	83
12		5	180	60	67
13		6	180	71	61
14		7	180	79	56
15	800Z30	1	180	50	72
16		2	180	22	88
17		3	180	11	94
18		4	180	34	81
19		5	180	58	68
20		6	180	68	62
21		7	180	83	54

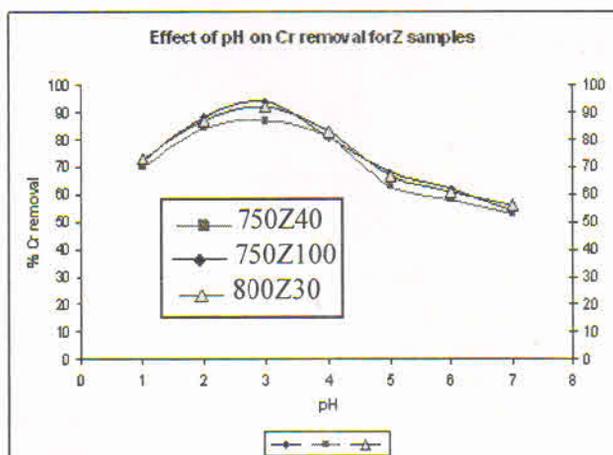
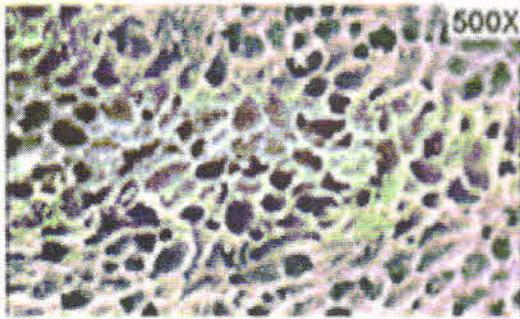
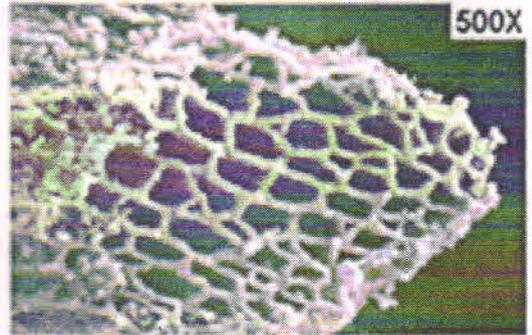


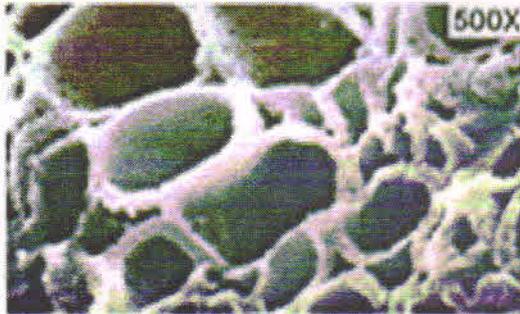
Fig. 3. Effect of pH on Cr removal for Z samples



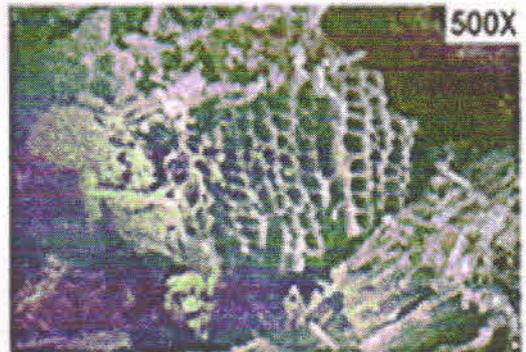
800Z30



800P30



750Z100



750P100

Fig. 4. SEM of 800Z30, 800P30, 750Z100 and 750P100 samples

mechanism for metal adsorption is due to the acidic functional C=O groups on the adsorbent surface. The presence of oxygen functional groups make the adsorbent surface negatively charged and therefore a repulsive electrostatic interaction between the adsorbent and the anion where as for a cation the negatively charged group enhances the electrostatic interaction with the negatively charged surface

of the adsorbent mainly through carboxylic ligands.

According to the figures 1, 2 and 3 the rates of adsorption are weak with low values of pH (<2). Between 2 and 3 the rates of absorption increase rapidly. This is due to the surface charge of the metal, which is strongly related to the pH of the solution. Maximum

adsorption capacity is observed in the pH range 2 to 3. This indicates that the pH corresponds to the zero point charge (pHzpc) which lies between the two values. The pHzpc is a point at which the adsorbent surface groups either acidic or basic no longer contribute to the pH of the solution². Maximum absorption of Cr (VI) ions at lower pH has been reported. In the present study it is observed that removal efficiency is maximum for samples that have been activated at higher temperatures or higher dwell time like 800Z30, 800P30, 750P100 or 750Z100. This is probably due to well formed and presence of uniform pores as observed in SEM study (Fig. 4).

Conclusions

In this investigation the employability of an abundantly available low cost material namely activated carbon from coconut shell for mitigating chromium (VI) pollution is investigated. Different routes for preparing good porous activated carbon have been identified.

The results obtained were analyzed for evaluating the use of carbon from coconut shells for chromium removal from solutions. The chromium removal was effective at a pH of 3 and removal efficiency was more than 95%. Optimum contact time has been found to be 50-60 minutes.

References

1. Min Gyu Lee, Gyeougheam Yi, Byoung Joon Ahu and Felicity Roddick-Conversion of Coal fly ash into zeolite and heavy metal

- removal characteristics of the products—*Korean Journal of Chem. Engg.* 17(3), 325-331 (2000).
2. Parinda Suksabye, Paitip Thiravetyan, Woranan Nakbanpote, Supanee Chayabutr-Chromium removal from electroplating wastewater by coir pith-online publication-Elsevier,doi 10.1010-2006.07.18
3. D. Mohan, K.P. Singh, 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.* 44, 1027–1042 (2005).
4. D. Petruzzelli, R. Passino, G. Tiravanti, Ion exchange process for chromium removal and recovery from tannery wastes, *Ind. Eng. Chem. Res.* 34, 2612–2617 (1995).
5. H. Shaalan, M. Sorour, S. Tewfik, Simulation and optimization of a membrane system for chromium recovery from tanning wastes, *Desalination* 14, 315–324 (2001).
6. Z. Song, C. J. Williams, R.G.J. Edyvean, Sedimentation of tannery wastewater, *Water Res.* 34 (7), 2171–2176 (2000).
7. V.K. Gupta, I. Ali, in: Somasundaran (Ed.), Adsorbents for water treatment: development of low cost alternatives to carbon for the updated 'Encyclopedia of Surface and Colloid science', *Marcel Dekker*, pp. 1–34 (2003).
8. V.K. Gupta, K.T. Park, S. Sharma, D. Mohan, Removal of chromium(VI) from electroplating industry wastewater using bagasse flyash-a sugar industry waste material, *Environmentalist* 19, 129–136 (1999).

9. S. Babel, T.A. Kurniawan, Low cost adsorbents for heavy metals uptake from contaminated water: a review, *J. Hazard. Mater. B* 97, 219–243 (2003).
10. D.E. Kimbrough, Y. Cohen, A.M. Winer, L. Creelman, C. A. Mabuni, Critical assessment of chromium in the environment, *Crit. Rev. Environ. Sci. Technol.* 29 (1), 1–46 (1999).
11. Z. Hu, L. Lei, Y. Li, Y. Ni, Chromium adsorption on high-performance activated carbons from aqueous solution, *Sep. Purif. Technol.* 31(1), 13–18 (2003).
12. E. Gonzalez-Serrano, T. Cordero, J. Rodriguez-Mirasol, L. Cotoruelo, J.J. Rodriguez, Removal of water pollutants with activated carbons prepared from H_3PO_4 activation of lignin from kraft black liquors, *Water Res.* 38, 3043–3050 (2004).
13. S. Babel, T.A. Kurniawan, Cr(VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan, *Chemosphere* 54, 951 (2004).