



Removal of Cr (VI) from contaminated water using efficient bioadsorbents

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Abstract

In an attempt to evaluate the suitability of non-conventional adsorbents such as activated carbon (AC), fly ash (FS), rice husk (RH) and saw dust (SD) for the removal of hexavalent chromium from wastewater, a comparative study was carried out using all these adsorbents. PAC, FA, SD and RH could remove 95.3, 77.6, 88.4 and 87.3% Cr (VI) at initial metal concentration 10 mg/l, Ph 6.0, temperature 25⁰C, agitation time 2 h and adsorbent dose 10 g/l. The order of metal removal capacities for these adsorbents was found to be: PAC > FA > SD > RH. The effect of various parameters affecting the adsorption such as initial metal concentration, adsorbent dose, contact time and pH was determined. Adsorption decreases with rise in metal concentration and pH but increases with increase in adsorbent dose and contact time. Equilibrium was attained in 1.5 h and the maximum removal was at pH 2. Thus, acidic medium favored the removal.

Key words: Bioadsorbents, heavy metal removal, contaminated water

Introduction

Hexavalent chromium Cr (VI) is used in various industries including metallurgy, chemical, chrome plating, manufacturing of stainless steel, dyes, ink and pigments, leather tanning and wood presser veng. It is also used in small amounts in drilling muds, rust and corrosion inhibitors, textiles and toner for copying machines. Because of its extensive use, chromium contamination of soil and water has become a prevalent problem. The most often observed oxidation states of Cr in natural water system are +3 and +6. Although trivalent chromium, is considered an essential trace element, Cr (IV) is toxic, carcinogenic, mutagenic and teratogenic. Cr (VI) exists in water as oxyanions such as chromate (CrO_4^{2-}), dichromate ($\text{Cr}_2\text{O}_7^{2-}$), and bichromate (HCrO_4^{2-}) whereas Cr (III) readily

precipitates as chromic hydroxide at pH values greater than 4. Reduction of Cr (IV) to Cr (III), Therefore, is often beneficial because a more toxic and mobile species of Cr is converted to a less toxic and Mobile form. Consequently two strategies for treatment of Cr (IV) in water can be considered: (1) removal of Cr(IV) by sorption (2) in situ precipitation and immobilization by reduction to Cr (III). Because conversion of Cr(IV) to Cr(III) may be desirable. Note that this second approach could still include reduction and precipitation steps after Cr VI) sorption has occurred.

Studies on the treatment of effluents bearing heavy metals and organics reveal sorption to be the most promising technique because it is highly effective, cheap, easy and ecofriendly method among all physicochemical processes. Sorption of (Alaerts et al.1989., Han et al. 2000., Hasar and Cuci, 2000.,) Cr (IV) by various materials has been studied by previous researchers. Though activated carbon is an ideal adsorbent for organic matter due to its organophilic character, it is not economical for wastewater treatment owing to its high production and regeneration costs, and about 10-15 % loss during regeneration by chemical or thermal treatment. High cost of activated carbon and synthetic resins in India has prompted search for cheaper substitute such as fly ash, saw dust, rice husk, peanut husk, banana peel, coir dust, waste tea leaves etc. are of the low cost adsorbents are used to removal of heavy metals.

Organics like phenolic compounds, chrome dyes, detergents, organic matter from distillery, sugar, paper and textile industries, herbicides like 3,4-dichlorophenoxyacetic acid etc. (Palanivelu et al., 1998). However, the comparative adsorption behavior of common adsorbents of Cr (IV) has not so far been studied, so the present study has been undertaken to investigate and compare the suitability powdered activated carbon (PAC), fly ash (FA), rice husk (RH) and saw duds (SD) for the Cr (IV) removal from wastewater using batch experiments. The study includes the effect metal concentration, contact time, sorbent dose and pH.

Materials and Method

Preparation of Cr (IV) Solutions

All reagents were analytical grade. In order to avoid interference by other elements in waste water, the experiments were conducted with aqueous solutions of hexavalent chromium in redistilled water. Synthetic samples of various initial Cr (IV) concentrations were prepared by dissolving potassium dichromate ($K_2Cr_2O_7$) in water. Four standard solutions of 1, 5, 10 and 20 mg/l concentrations of Cr (IV) were prepared by diluting the stock solution that was made by dissolving

2.829 g $K_2Cr_2O_7$ in double distilled water and adding 20 ml HNO_3 and diluting to 1 liter (1000 mg/l).

Preparation of adsorbents

Natural and easily available like AC, FA, SD and RH were used as adsorbents (Talokar et al., 2001) for the metals. PAC was prepared from coconut coir husk treated with not distilled water and dried at $100^{\circ}C$, then reacting 50 g of the product so obtained with 50 ml of concentrated H_2SO_4 , then it was carbonized at $150^{\circ}C$ for 12 hours. The

sorbent was dried and ground to increase the surface area. The particle size of 100 mesh ASTM was determined with a standard test sieve. FA was bagasse flyash from a Harduaganj Thermal Power Plant, Aligarh. RH and SD were obtained from local factories. Adsorbents were analyzed using standard method and their properties are presented in Table 1.

Table 1. Characteristics of adsorbents

Characteristics	PAC	FA	SD	RH
Density (g/cc)	2.50	3.40	2.69	2.69
Bulk density (kg/m ³)	750.82	370.53	560.00	310.20
Moisture (%)	0.31	9.61	15.00	8.20
Ash (%)	2.65	30.32	12.32	2.30
Volatile matter (%)	7.74	29.39	14.08	10.02
Combustible matter (%)	84.16	74.85	86.54	89.02
Loss of ignition	3.02	11.83	12.96	9.02
Chemical analysis				
SiO ₂ (%)	8.00	61.05	22.92	91.35
Al ₂ O ₃ (%)	2.02	16.05	12.44	1.83
CaO (%)	0.12	3.04	4.15	1.35
Fe ₂ O ₃	1.32	5.23	2.26	2.51
MgO (%)	1.02	1.10	2.36	1.04
Surface area (m ² /g)	530.00	280.00	228.00	198.00

Batch Studies

The interaction studies were carried out in batch tests. In 8 numbers of 250 ml capacity glass bottles, 10 g/l of adsorbent was added to each of four sets each having two bottles for one concentration and 100 ml of the metal solution was added to each bottle. The bottle was shaken in a reciprocating shaker at a rate of 100 forward and backward displacements per minute for 3 hours at room temperature. Then the contents were centrifuged at 3000 rpm for 10 minutes and the supernatant liquid was filtered using Whatman 42 filter paper. The filtrate was used for the Cr (IV) determination. The results in duplicate were averaged for each feed concentration. The uptake of metal on the sorbent at different concentrations of initial feed was thus calculated and depicted in Fig. 1. To study the effects of adsorbent dose 1, 5, 10, 15, and 20 g sorbent/l of metal solution, and the effects of pH on sorption pH values 2, 4, 5, 6 and 8 of the mediums were taken.

Results and Discussion

Effect of Initial Concentration and Contact Time

Sorption capacity is found to decrease with increase in metal concentration. The higher uptake at lower initial concentration can be attributed to the availability of more isolated metal ions. Sorption rate is very rapid during initial period of contact and about 82 percent of sorption is reached with first 30 minutes. However, equilibrium was attained within 1.5 h. PAC, FA, SD and RH could remove 95.3, 83.5, 77.6, 88.4 and 87.3% Cr (IV) at initial metal concentration 10 mg/l, pH 6.0, temperature 25⁰C, agitation time 2 hour and adsorbent dose 10 g/l. The order of metal removal capacities for these chemical adsorbents was found to be PAC>FA>SD>RH. The effect of various parameters affecting the adsorption such as initial metal concentration, adsorbent dose, contact time and pH was determined. Adsorption decreases with rise in metal concentration and pH but increases with increase in adsorbent dose and contact time.

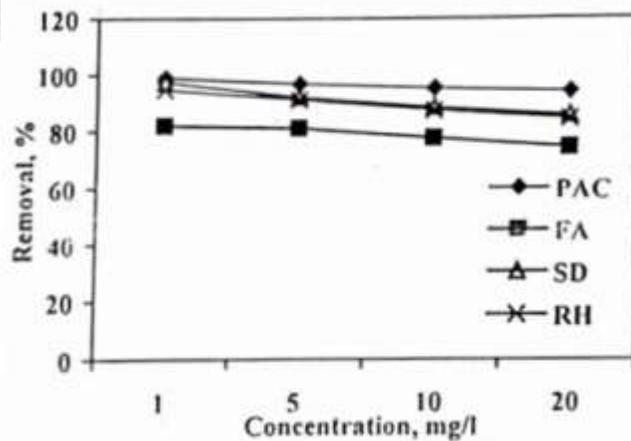


Fig. 1 Effect of Cr (IV) concentration on its % removal at pH 6.0, temperature 25⁰C, agitation time 2 hours and adsorbent dose 10 g/l

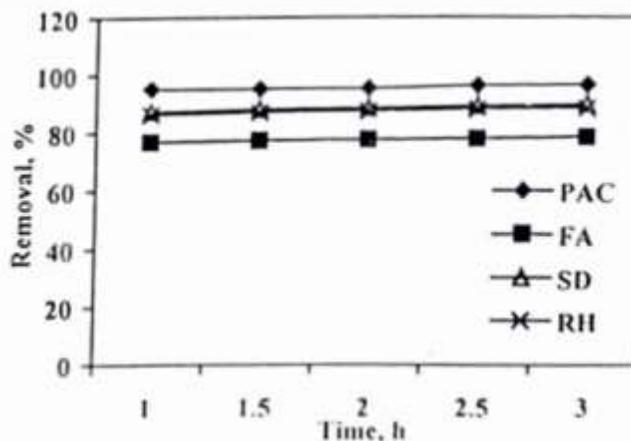


Fig. 2. Effect of contact time on % removal at Cr (IV) concentration 10 mg/l pH 6.0, temperature 25⁰C and adsorbent dose 10 g/l

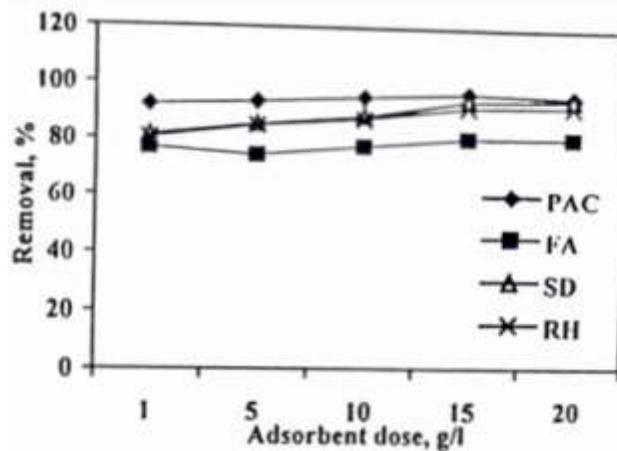


Fig. 3. Effect of adsorbent dose on % removal at Cr (IV) concentration 10 mg/l, pH 6.0, temperature 25°C and contact time 2 hours

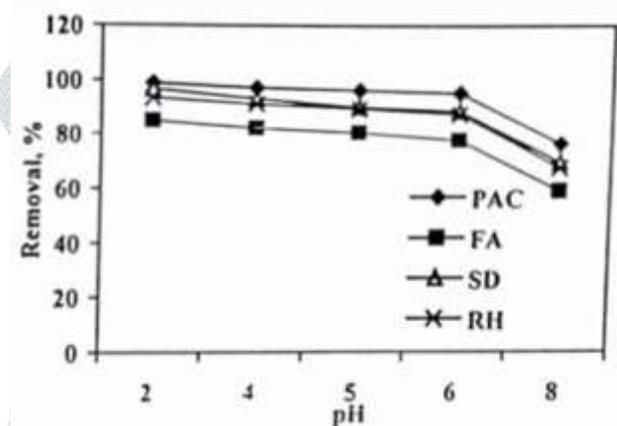


Fig. 4. Effect of pH on % removal at Cr (IV) concentration 10 g/l, temperature 25°C, contact time 2 hours and adsorbent dose 10 g/l

Effect of adsorbent Dose

The effect of adsorbent dose on the adsorption of Cr (IV) using different adsorbents at pH 6 and temperature 25°C is depicted in Fig. 3. It clearly indicates that the percent Cr (IV) removal increase with increase in adsorbent dose. It is obvious from this graph that as the sorbent dose is increased, percent metal removal also increases, but after an optimum dose of 15 g sorbent dose is increased, percent metal removal also increases, but after an optimum dose of 15 g sorbent per liter of metal solution there is no appreciable change in removal. Further, at lower sorbent dose, the adsorbate is more easily accessible and because of this, removal per unit weight of adsorbent is higher. The initial rise in adsorption with adsorbent or adsorbate concentration is probably due to bigger driving force and lesser surface area. Larger surface area of sorbent and smaller size of adsorbate favor adsorption. The rate of adsorption is high in the beginning as sites are available and unimolecular layer increases. Adsorption and desorption occur together and rates become equal at a stage called adsorption equilibrium when isotherms are applied. That is why there is little increase in % removal on increasing adsorbent dose from 15 to 20 g/ml of Cr (IV) solution. The subsequent slow rise in curve may be due to adsorption and intra-particle diffusion taking place

simultaneously with dominance of adsorption. With rise in sorbent dose there is less commensurate increase in adsorption resulting from lower adsorptive capacity utilization of sorbent. This is called ‘solid concentration effect’ meaning overcrowding of particles.

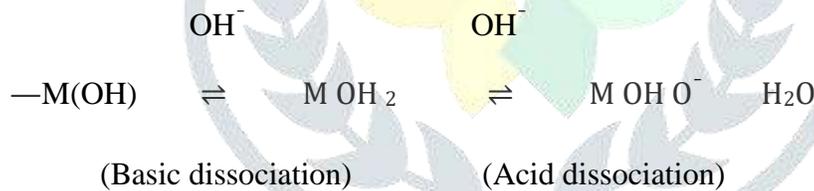
Effect of pH

100 ml solution of 10 mg/l Cr (IV) concentration was adjusted pH 2 to 8 with HCl/NaOH and treated with 1g of sorbent and 2-h agitation. The influence of pH of solution on the extent of adsorption of metals is depicted in Fig. 4. The Cr (IV) removal is highly dependent on pH of the medium, which effects the surface charge of the adsorbent and degree on ionization. The maximum removal was at pH 2. Thus, acidic medium favored the removal.

Fly ash mainly consist of oxides of silicon, aluminum, iron, calcium, magnesium etc. many researchers have found that anion adsorption sites on such minerals like alumina and clay are aquo groups (—M—OH_2 and hydroxy groups (—M—OH). The surface chemistry of an oxide in contact with an aqueous solution is determined to a large extent by deprotonation or a hydroxyl ion association reaction. However, some evidences suggest that an anion like Cr_2O_7^- can be adsorbed by ion exchange mechanism even though the surface is neutral.



The presence of oxides of alumina, calcium and silicon of the adsorbents develop charge in contact with water according to pH of the solution as follows:



In the present study, the optimum pH for metal removal was found in the acidic medium. The reason may be attributed to the large number of H^+ ions in acidic medium neutralize negatively charged adsorbent surface, thereby reducing hindrance to diffusion of dichromate ions at higher pH the abundance of OH^- ions create increased obstacle to diffusion of dichromate ions. Above and below this pH, the extent adsorption was considerably low. Except silica, all other oxides (the major constituent of flyash being alumina) possess positive charge for a pH range of interest. As the pH decreases below 4.5, Al_2O_3 is dissolved as Al^{3+} and subsequently the surface of Al_2O_3 becomes further positively charged with decrease in pH. As pH increases, the hydro group (—M—OH) goes on disappearing and forming increasingly negatively charged surface. In addition, OH also competes for the available sites left on the surface.

The zero-point charge of SiO_2 , Al_2O_2 and CaO are 2.2, 8.3 and 11.0 respectively. Thus, the negatively charged silica surface sites of adsorbents get neutralized by H^+ ions thereby reducing hindrance to diffusion of anions present in the aqueous phase.

The maximum adsorption of metals takes place in acidic solution at about pH 2. The reason for high adsorption at very low pH may be attributed to the large number H^+ ions present at low pH values which in turn neutralize negatively charged adsorbent and adsorbate surfaces, thereby increasing the sorption.

Conclusions

The following conclusions can be drawn from the above results: PAC, FA, SD and RH could remove 95.3, 77.6, 88.4 and 87.3% Cr (IV) at initial metal concentration 10 mg/l, pH 6.0, temperature 25⁰C, agitation time 2 hours and adsorbent dose 10 g/l. The order of metal removal capacities for these chemical adsorbents was found to be PAC>FA>SD>RH. The effect of various parameters affecting the adsorption such as initial metal concentration, adsorbent dose, contact time and pH was determined. Adsorption decreases with rise in metal concentration and pH but increases with increase in adsorbent dose and contact time. Equilibrium was attained in 1.5 hours and the maximum removal was at pH 2. Thus, acidic medium favored the removal.

References

1. Dias M., Pinto J., Henriques B., Figueria P., Fabre E., Tavares D., Valec and Pereira E., (2021) Nutshell as efficient biosorbents to removal cadmium, lead and mercury from contaminated solutions. *Inter. J. Environ. Res. Public Health*, vol.8(4), p. 1580
2. Arthur D.E., and Oyibo A.A., (2021) Application of Taguchi design in the removal of heavy metals from simulated metal solutions using groundnut shell and tea bag as a natural adsorbent. *of the National Research center*. 45:14
3. Merchant R.R., and Painter Z.Z., (2019) Study of removal of heavy metals from waste water by adsorption. *International J. of Applied Eng., Research* ISSN 0979-4562
4. Nurain A., Sarkar P., Rahaman M.S., Rahman M.M., and Uddin M.K., (2021) Utilization of banana (*Musa Sapientum*) peel for removal of Pb^{+2} from aqueous solution, *Journal of Multidisciplinary Applied natural Science*. Available at [http s://ssrn.com/abstract-3897232](http://ssrn.com/abstract-3897232)
5. Ashraf M.A., Vajid A., Mahmood K., Jamilmaah M.,and Yousoff I.,(2011) low cost biosorbent banana peel (*Musa Sepientum*) for the removal of heavy metals. *Scientific Research and Essays* vol.6(19), p. 4055-4064
6. Mohamed M.,Rabiatul H., Norazlina N., Abdullah S., Abdullah A., Nabihan M., Amri A.

- A. A.D.M., and Fakrul A.M.K., (2020) Adsorption of heavy metals on banana peel bioadsorbent. Journal of Physics conference series, vol. 1532, issue 1, article id- 012014
7. Alaerts G .J JiljaUiaranl V. and Kclderman I., (1989) Use of coconut shell based activated carbon for chromium(VI) removal, Wat. Res. Technol 21 1901
 8. CiminoG., Passerini A. and Toscano G. (1999), Removal of toxic from aqueous solution by hazelnut shell, Wat. Res., 34(11), 2955-2962
 9. Han 1., Schlautman M.A. and Batchelor B., (2000) Removal of hexavalent chromium from groundwater by granular activated carbon, Wat. Environ. Res., 72, 29-38
 10. Haribabu E., Upadhyay S.N. and Upadhyay Y.D., (1992) Removal of chromium VI) by flyash, Chem. Environ. Pes., 1(3), 289-294
 11. Hasar, H. and Cuci,Y., (2000) Removal of Cr(VI), Cd(II) and Cu(II) by activated carbon prepared from almond husk, Environmental Technology, 21, 1337-1342
 12. Jasuja K., Parwana H.K. and Rao A.L.J., (1997) Removal of Cr (VI) from wastewater by *Ablesmoschus eseulentus*, 1JEH, 39(2), 103-108
 13. Manju G.N. & Anirudhan T.S., (1997) Use of coconut fiber pith-based pseudo-activated carbon for chromium (VI) removal, Ind. J. Environ. Hlth., 39(4), 289-298
 14. Palanivelu K., Lakshmi D.S. and Ranganathan K.R., (1998) Removal and recovery of hexavalent chromium from plating wastewater using liquid membrane, J. of Scientific and cations and Cr (VI) Industrial Research, 57, 903-906
 15. Rai A.K. and Kumar S., (1999) Treatment of chromium bearing waste water by adsorption brickkiln ash and flyash, Ind. J. Environ. Hlth., 41(1), 65-73
 16. Singh R.P., Singh Y., Swaroop D., Gupta N. and Singh S. (2001) Comparison of activated carbon, fly ash, rice husk and saw dust for the removal of Cr, Zn, Cd and Pb from waste water, Procs., RAWM-2001, IAEM, 285-289
 17. Srinivasan K., Balasubramanian N. & Ramakrishnan T.V., (1988) Studies on chromium removal by rice husk carbon, Ind. J. Environ. Hlth., 30, 376
 18. Sujatha K.M., Kumar S. and Upadhyay S.N., (1995) Chromium (VI) removal by spent myrobalan nuts, IAEM, 22, 247-248
 19. Talokar A .Y., Ingole N . W., Rao M., (2001) Studies from the removal of chromium from wastewater by adsorption using low-cost adsorbents, Procs., RAWM-(2001), IAEM, 291 296