

Adsorption of chromium from aqueous solution by activated alumina and activated charcoal

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Abstract

Cr (VI) is considered to be potentially carcinogenic to humans. Removal of Cr (VI) ions from aqueous solution under different conditions was investigated using activated alumina (AA) and activated charcoal (AC) as adsorbents. Batch mode experiments were conducted to study the effects of adsorbent dose, contact time, pH, temperature and initial concentration of Cr (VI). Results showed that the adsorption of Cr (VI) depended significantly on pH and temperature. Equilibrium studies showed that Cr (VI) had a high affinity for AA at pH 4 and AC at pH 2. For AA, maximum adsorption was found at 25°C, indicating exothermic adsorption, while for AC, maximum adsorption was at 40°C. Freundlich and Langmuir adsorption isotherms were also applied and they showed good fits to the experimental data. The results suggest that both AA and AC could be used as effective adsorbents for the removal of Cr (VI) ions.

Keywords: Activated alumina, activated charcoal, adsorption, Cr (VI), temperature.

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Introduction

Chromium (Cr) is found naturally in rocks, soil, plants, animals, volcanic dust and gases. It is present in aqueous solution mainly in Cr (III) and Cr (VI) oxidation states. Cr (VI) salts show higher mobility than Cr (III) and hence are considered to be more toxic to humans (ATSDR, 1998). Cr enters water bodies from industries such as electroplating, leather tanning, cement, steel, paint, ink, dyes, aluminium and textiles. It can also percolate into the soil by leaching and has the potential to contaminate groundwater, which can be a major source of drinking water (IARC, 1987; ATSDR, 1998).

In view of the health problems caused by Cr (VI), the present study was performed to evaluate activated charcoal (AC) and activated alumina (AA) as adsorbents for the removal of Cr (VI) from polluted water by systematic evaluation of the parameters involved such as pH, Cr concentration, time, adsorbent dose and temperature. Furthermore, the Freundlich and Langmuir adsorption isotherms were applied to study the kinetics of adsorption and to calculate isotherm parameters.

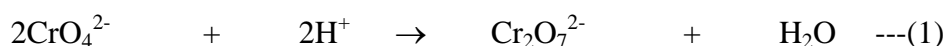
Materials and Methods

All the reagents used were of AR grade. Stock and subsequent solutions of Cr (VI) were prepared by dissolving $K_2Cr_2O_7$ in double distilled water. Granular activated alumina (Grade AD, 101- IPCL, India) and activated charcoal (S.D. Fine Chemicals, Mumbai, India) were used as such without further grinding and sieving. The properties of these adsorbents used for Cr (VI) removal are listed in Tables 1 and 2. Batch experiments were conducted to understand the mechanism for the removal of Cr (VI) by AA and AC and all the experiments were conducted under constant shaking of 100 ml of simulated Cr (VI) wastewater in a conical flask of 250 ml. Samples were withdrawn after a definite time interval and filtered through Whatman No. 1 filter paper (0.45 μ m). The filtrates were analysed for residual Cr (VI) concentration by reaction with 1,5-diphenylcarbazide followed by absorbance measurement at 540 nm using a UV-visible spectrophotometer (ELICO-SL-150).

Results and Discussion

Influence of Solution pH

The effect of pH was determined by studying adsorption of Cr (VI) at initial Cr (VI) concentration of 10 mg/l with adsorbent doses of 1g/100ml for AA and AC over a pH range of 2 to 10. pH adjustments were made either with 0.1N HCl or 0.1N NaOH. The effect of pH on the adsorption of Cr (VI) by AA and AC is shown in Figure 1, which shows that maximum adsorption for AA was observed between pH 4 (99%) and pH 6 (95%), with decreasing values on either side of this pH range. For AC, maximum adsorption was noticed at pH 2 (99%) and at pH 4 (92%). pH dependence of metal adsorption can largely be related to type and ionic state of the functional group present in the adsorbent and also to the metal chemistry in the solution (Gupta et al., 2001). High adsorption of Cr (VI) at low pH can be explained by the species of the Cr and the adsorbent surface. At acidic pH, the predominant species of Cr are $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- , $\text{Cr}_3\text{O}_{10}^{2-}$ and $\text{Cr}_4\text{O}_{13}^{2-}$ (Weckhuysen et al., 1996; Raji and Anirudhan, 1998) and above pH 8, only CrO_4^{2-} is stable and as the pH decreases into the region 3 - 6, the equilibrium shifts to dichromate according to the overall equilibrium.



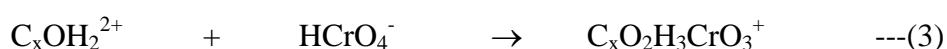
At still lower pH values, $\text{Cr}_3\text{O}_{10}^{2-}$ and $\text{Cr}_4\text{O}_{13}^{2-}$ species are formed. Thus, decreasing pH results in the formation of more polymerised Cr oxide species. On the other hand, under acidic conditions, the surface of the adsorbent becomes highly protonated and favours the uptake of Cr (VI) in the anionic form. With increase in pH, the degree of protonation of the surface reduces gradually and hence adsorption is decreased (Selvi et al., 2001). Furthermore, as pH increases there is competition between OH^- and chromate ions (CrO_4^{2-}), the former being the dominant species at higher pH values. The net positive surface potential of sorbent decreases, resulting in the weakening of electrostatic forces between sorbent and sorbate, which ultimately leads to reduced sorption capacity.

In the present study, equilibrium solution pH was found to increase. The resultant equilibrium pH is shown in Table 3 with an initial Cr (VI) concentration of 10 mg/l and adsorbent does of 1g/100ml for each adsorbent ie. AA and AC.

Increase in pH can be explained by solute - sorbent binding reactions. When the oxo groups (C_xO and C_xO_2) present on the surface of carbonaceous material come into contact with water, they react with the water molecule as follows:



Thus, hydroxyl ions released into solution raise the equilibrium pH. When Cr (VI) ions are introduced into the system, they are absorbed onto the positively charged surface.



Combining equation (2) and (3) gives



Hence, every mole of $HCrO_4^-$ adsorbed results in the release of two moles of hydroxyl ions into solution, which eventually raises the solution pH. In addition, reaction (1) is also a proton-consuming reaction. Thus, the removal of protons from solution also results in an increase in pH.

The high pH value causes a reduction in the electrostatic attraction between negatively charged Cr ions and positively charged adsorbent surfaces, therefore reduced percent removal was observed at high pH.

Influence of Temperature

Adsorption experiments were run at 25, 30, 40 and 50°C to investigate the effect of temperature with an initial Cr (VI) concentration of 10 mg/l and adsorbent dose of 1g/100ml for both adsorbent. For AA, it was observed that adsorption decreased with increase in temperature and was found to reach a maximum at 25°C, indicating an exothermic adsorption. The temperature effect is the net effect of temperature on the Cr (VI) – oxide bond, the water-alumina bond, the Cr (VI) - Cr (VI) interactions and the water – Cr (VI) interaction. The water - alumina bond is important, as adsorption of Cr (VI) probably involves

concomitant displacement of water molecules from the alumina surface. For AC, maximum adsorption was found at 40°C and there was a decrease in adsorption with decreasing temperature. This can be explained by the fact that at lower temperature the kinetic energy of $\text{Cr}_2\text{O}_7^{2-}$ anions is low, therefore contact between $\text{Cr}_2\text{O}_7^{2-}$ and the active sites of AC is insufficient, leading to a decrease in adsorption efficiency. Furthermore, at higher temperature, the kinetic energy of the $\text{Cr}_2\text{O}_7^{2-}$ anion is higher than the attraction potential between $\text{Cr}_2\text{O}_7^{2-}$ and active sites in AC. This condition causes a decrease in adsorption efficiency, showing that adsorption is more of a physical than a chemical property. This view is supported by the findings of Daneshvar et al. (2002).

Influence of adsorbent dose and contact time

To optimise the adsorbent dose and time for the removal of Cr (VI) from the solution, adsorption studies were carried out at initial Cr (VI) concentration of 10 mg/l with different adsorbent doses at different time intervals (15 to 180 min). Measurement of percentage Cr (VI) adsorption as a function of time at different doses indicated that sorption of Cr (VI) increased with increasing dose of AA and AC. Increase in adsorption with dose can be attributed to increased surface area and the availability of more binding sites for adsorption. Furthermore, time taken to reach apparent equilibrium was reduced at the higher doses of adsorbents. For AA, sorption of Cr (VI) attained a maximum after 90 minutes and thereafter was almost constant up to the studied time of 180 minutes. The removal of Cr (VI) by AA ranged from 97.3% to 99.7% at 90 min time with various adsorbent doses of 0.5 g/ 100 ml to 1.0 g/100 ml. The removal of Cr (VI) by AC ranged from 68% to 98% with various doses of 0.1 to 5.0 g/100ml. For AC, equilibrium time was 120 minutes and after that percentage removal was more or less constant. Therefore, it can be concluded that the rate of Cr (VI) binding with adsorbent was greater in the initial stages, then gradually decreased and remained almost constant after an optimum period.

Influence of initial Cr (VI) concentration

Adsorption experiments at initial Cr (VI) concentrations from 10 to 100 mg/l were also performed with fixed doses (1g/100ml) of AA and AC. The results indicated that percentage Cr (VI) removal decreased as the initial concentration of

Cr (VI) was increased. For AA, Cr (VI) removal ranged from 99.8% to 76.94% at initial Cr (VI) concentration of 10-100 mg/l (Figure 2). This can be explained by the fact that all the adsorbents had a limited number of active sites, which would have become saturated above a certain concentration. For AC, removal was 99% at various initial concentrations of Cr (VI) ranging from 10-100 mg/l, so AC was found to be very efficient in Cr (VI) removal.

Adsorption isotherms

The distribution of Cr (VI) between the liquid phase and the solid adsorbent phase is a measure of the position of equilibrium in the adsorption process and can be expressed by the most popular isotherm models. The data was fitted to Freundlich and Langmuir equations in linear form.

The Freundlich equation has the following form

$$\log(q) = \log(k) + \left[\frac{1}{n} \right] \log C_e \quad (1)$$

Where q is the amount of solute adsorbed per unit weight (mg/g) of the adsorbent used, C_e is the equilibrium solute concentration in the solution (mg/L) and k and n are the constants representing the adsorption capacity (mg/g) and intensity of adsorbent respectively. The values of k and n were obtained from the slope and intercept of a plot of $\log(q)$ versus $\log C_e$ and are reported in Table 4. Both of the parameters k and $1/n$ affect the adsorption isotherm. The larger the k and $1/n$ value, the higher the adsorption capacity.

The Langmuir equation was also applied to quantify adsorption capacity and is given below

$$\frac{C_e}{q} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (2)$$

Where C_e and q are the equilibrium solute concentration in the solution (mg/L) and equilibrium adsorption capacity, respectively. q_m and b are the Langmuir constants representing adsorption capacity and energy of adsorption (L/mg), respectively. The values of q_m and b were obtained from the slope and intercept of a plot of C_e versus C_e/q and are reported in Table 4. The larger the constant b , the higher is the adsorption energy, reflected by a fast increase in adsorption at low concentrations of adsorbate. Further experimental values and

calculated values are shown in Figure 3, obtained from Freundlich and Langmuir isotherms and it yield R^2 values of 0.7979 and 0.8937 respectively for AA and AC.

Conclusions

AA and AC were found to be suitable adsorbents for the removal of Cr (VI) from aqueous solution. The adsorption was found to be strongly dependent on pH, adsorbent dose, contact time, initial Cr (VI) concentration and temperature. The adsorption process for AA was found decrease with increasing temperature, showing the exothermic nature of the adsorption. The uptake of Cr (VI) by AA was maximum at pH 4 while for AC this occurred at pH 2. Furthermore, the results obtained in this study showed good fits to the Freundlich and Langmuir adsorption isotherms. These adsorbents could be used effectively for the removal of Cr (VI) from polluted water.

Acknowledgement

The authors express their thanks to Professor Julian AS Goodwin for his valuable editorial cooperation.

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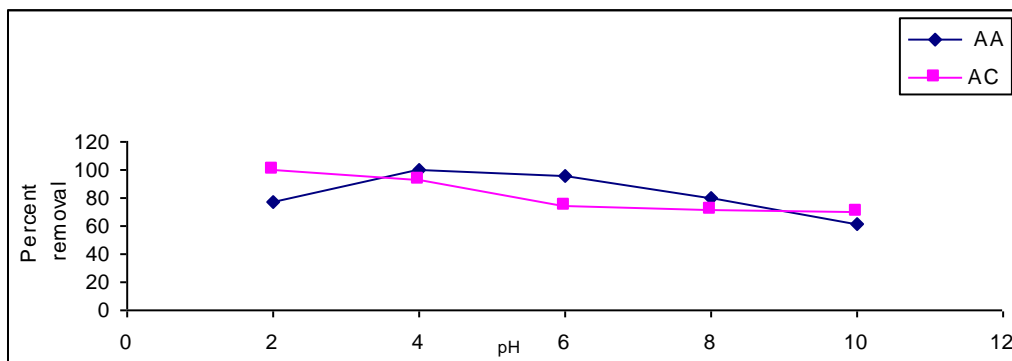


Figure 1: Effect of pH on percent removal of Cr (VI) by AA and AC

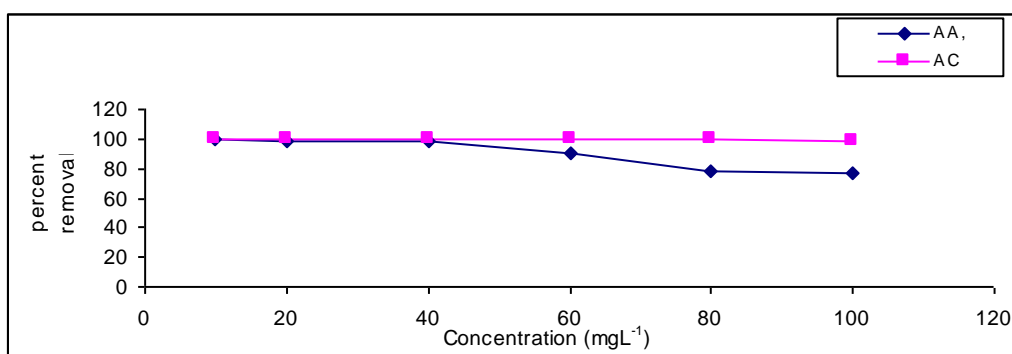


Figure 2: Effect of initial concentration on percent removal of Cr (VI) by AA and AC

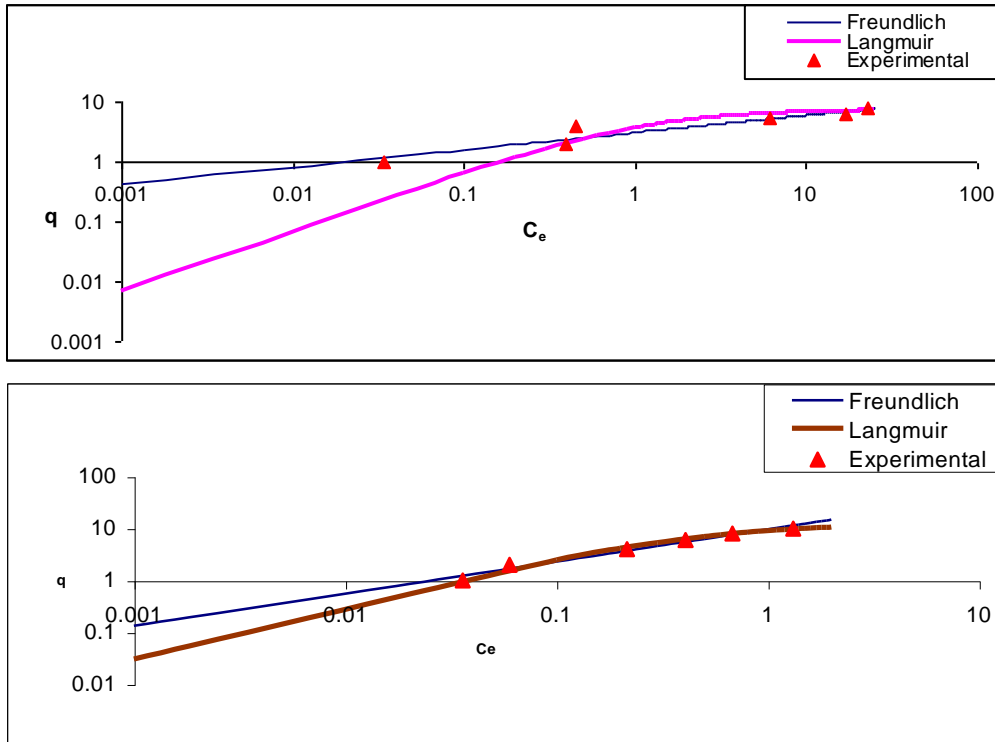


Figure 3: Plot of experimental and calculated values from Freundlich and Langmuir isotherms for AA (above) and for AC (below)

Table 1: Properties of activated alumina (Grade Ad-101).

Properties	Quantitative value
Surface area ($\text{m}^2 \text{g}^{-1}$)	370
Particle size (spherical mm)	2.0 ± 0.1
Pore volume (ml g^{-1})	0.42
Bulk density (kg m^{-3})	800
Loss on attrition (%)	0.2
Al_2O_3 (%)	93.1
Na_2O (%)	0.02
Fe_2O_3 (%)	0.04
SiO_2 (%)	0.03

Table 2: Properties of activated charcoal.

Properties	Quantitative value
Raw material	Coconut shell
Surface area ($\text{m}^2 \text{g}^{-1}$) (based on BET)	1000
Bulk density (kg m^{-3})	500
Particle density (kg m^{-3})	850
Ash content (on dry basis) (%)	3.59
Moisture content (%)	5.0
pH_{ZPC}	5.3
Conductivity ($\mu\text{S cm}^{-1}$)	94.0
Particle size	8–20 mesh

Table 3: Initial and Equilibrium Solution pH for AA and AC

Initial pH	Equilibrium pH (AA)	Equilibrium pH (AC)
2	2	2
4	5.6	6.9
6	6.6	7.4
8	7.2	7.5
10	7.6	7.5

Table 4: Adsorption isotherm constants for Cr (VI) on AA and AC

Isotherm Constants				
Adsorbents	K (mg/g)	n	q_m (mg/g)	b (l/mg)
AA	3.1262	3.438	7.44	0.9451
AC	0.9614	1.6162	12.87	2.369