



Hexavalent chromium [Cr(VI)] removal by acid modified waste activated carbons

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ABSTRACT

Fresh activated carbon (AC) and waste activated carbon (WAC) were pretreated by heating with mineral acids (sulfuric acid and nitric acid) at high temperature to prepare several grades of adsorbents to evaluate their performance on Cr(VI) removal from aqueous phase. Effects of temperature, agitation speed and pH were tested, and optimum conditions were evaluated. Kinetic study was performed under optimum conditions with several grades of modified adsorbents to know the rates of adsorption. Batch adsorption equilibrium data followed both, Freundlich and Langmuir isotherms. Maximum adsorption capacity (q_{max}) of the selected adsorbents treated with sulfuric acid (MWAC 1) and nitric acid (MWAC 2), calculated from Langmuir isotherm are 7.485 and 10.929 mg/g, respectively. Nitric acid treated adsorbent (MWAC 2) was used for column study to determine the constants of bed depth service time (BDST) model for adsorption column design.

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1. Introduction

Water pollution by chromium is due to both, natural sources and man made activities. Chromium is found in rocks, animals, plants, soils and in volcanic dusts and gases. Various industrial processes such as steel production, electroplating, leather tanning, nuclear power plant, textile industries, wood preservation, anodizing of aluminum, water-cooling and chromate preparation discharge chromium containing wastes with varied concentrations between 5 and 220 mg/L into the environment, which contaminates soil and water [1–3]. Chromite world mine production was estimated at a gross mass of 13×10^6 metric tons in 2002 [4]. In nature chromium exists in two most stable oxidation states, i.e., trivalent and hexavalent forms in aqueous systems. Although, at trace level the trivalent form is considered as an essential nutrient [5–6], hexavalent form of chromium is toxic, carcinogenic and mutagenic in nature [7–12]). The hexavalent form is about 500 times more toxic than the trivalent form [13]. Furthermore, Cr(VI) is highly mobile in soil and aquatic system, and also is a strong oxidant capable of being adsorbed by the skin [14]. Considering its toxic and carcinogenic nature, the maximum levels permitted for trivalent chromium in wastewater are 5 mg/L and for hexavalent chromium are 0.05 mg/L [15–16]. The most common methods of Cr(VI) removal from aqueous system are chemical precipitation, ion exchange, membrane processes, electro dialysis

and adsorption [17–20]. Hexavalent chromium usually exists in wastewater as oxyanions such as chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) and does not precipitate easily using conventional precipitation methods. Ion exchange, reverse osmosis, and electro dialysis are efficient for Cr(VI) ion removal but the cost is relatively high [20]. Furthermore, chromium removal techniques such as co-precipitation, membrane techniques and solvent extraction are challenged by the removal of lower concentrations of metals from solution [21]. On the other hand, activated carbon is effective for the removal of various heavy metal ions from industrial wastewaters. However, high cost of activated carbon encourages using of low cost and/or waste materials as adsorbent for various pollutant removals from aqueous environment [22–27]. It has been reported that surface modification with suitable chemicals and impregnation techniques not only increase adsorption capacity but also add selectivity to carbon [28–35].

In the present investigation, performance of acid modified waste activated carbon on Cr(VI) removal is investigated.

2. Materials and methods

All the chemicals used in the present investigation were either of analytical reagent (AR) or laboratory reagent (LR) grades. Potassium Dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) with 99% purity was used to prepare synthetic chromium containing wastewater. The adsorbent used in the present study is in fact a waste material. Eureka forbs Ltd. as well as others manufacture/market water purifiers in India with various brand names such as Aqua Guard. Depending upon the size and capacity of the unit, such water purifiers contain 200–300 g of

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Table 1
Details of various adsorbents.

Designation	Pretreatment employed
AC	Modification of activated carbon with distilled water
WAC	Modification of waste activated carbon with distilled water
MAC 1	Modification of AC with sulfuric acid (H ₂ SO ₄) (3:4 ratio, by mass) at 160 °C
MWAC 1	Modification of WAC with sulfuric acid (H ₂ SO ₄) (3:4 ratio, by mass) at 160 °C
MAC 2	Modification of AC with 7 mol/L of HNO ₃ at 90 °C
MWAC 2	Modification of WAC with 7 mol/L of HNO ₃ at 90 °C

activated carbon, impregnated with 0.2% silver. The uniform grain size of fresh activated carbon is in the range of 2–3 mm. The useful life of the adsorbent varies from 6 months to 1 year, and it is then replaced by fresh activated carbon. This waste activated carbon is then thrown away as a solid waste. This solid waste, designated as raw waste activated carbon, was collected, regenerated, and its adsorption capacity on Cr(VI) removal from wastewater was evaluated in the laboratory. The same grade of fresh activated carbon, before its use in water purifier, was also collected and used for further study.

The activated carbons (fresh and waste) were pretreated to modify by acid treatment, by following partly, the procedure suggested by Liu et al. [34] and Valix et al. [21], before evolution of their adsorption behavior. Above described 20 g of each of the adsorbents (fresh and waste activated carbons) were washed 3–4 times with 200 mL deionized water. The adsorbents were kept in a hot air oven for 10 h at a temperature of 110–120 °C to remove moisture and any readily volatile materials present on the surface and within the pores of the grains. After cooling to room temperature, the above distilled water treated adsorbents were designated as activated carbon (AC) and waste activated carbon (WAC), respectively. Ten grams of each of the above adsorbents (AC and WAC) were digested with concentrated sulfuric acid (with 3:4 ratio, by mass) for 2 h at 160 °C [21]. These new modified activated carbons are designated as MAC 1 and MWAC 1. In another modification process, 10 grams of each AC and WAC were immersed in 50 mL of 7 mol/L nitric acid (HNO₃) in a 100 mL glass beaker. The contents were slowly stirred with the help of magnetic stirrer for a period of 12 h at a temperature of 90 °C [34]. The remaining nitric acid in the beakers was discarded and the adsorbents were kept inside a hot air oven for 10–12 h, at a temperature of 110–120 °C. After cooling, the acid treated adsorbents were designated as modified activated carbon (MAC 2) and modified waste activated carbon (MWAC 2), respectively. The details of the adsorbents, used in the present study, are given in Table 1.

2.1. Analytical method

pH of the solution was measured by using digital pH meter (Model: μ pH system-361, India). Chromium (total) was measured in Atomic Absorption Spectrophotometer (AAS) (Model, AA 55; Varian Inc., USA). Chromium(VI) and total chromium were measured as per the procedure suggested in *Standard Methods* [36] by colorimetric method using a spectrophotometer (Model: Systronics, India) at the λ_{\max} of 540 nm. Chromium(III) was calculated by subtracting the amount of Cr(VI) from total chromium, wherever felt necessary.

2.2. Kinetic study and screening of adsorbents

All the six grades of adsorbents (Table 1) were considered for kinetic study. A specified amount of carbon (0.2 g) was added into

a series of 250 mL conical flasks, containing 100 mL of 10 mg/L of Cr(VI) solutions. The pH of the mixtures was adjusted to 2.0 with the help of HCl and NaOH solutions to conduct test below isoelectric point. The mixtures were then stirred in an incubator shaker at controlled temperature of 28 °C (~room temperature) for a maximum period of 12 h at an arbitrarily selected agitation speed of 130 rpm. The samples were taken at different time interval in self scarifying mode, filtered through filter paper (Whatman No. 40), and analyzed for residual Cr(VI) concentration, following the procedure explained in the previous section. A sample containing no adsorbent was also run as a “Blank”.

2.3. Effects of temperature, agitation speed and pH

Based on the kinetic study, only MWAC 1 and MWAC 2 adsorbents were considered for the determination of optimum temperature, agitation speed and pH. A specified amount of 0.2 g of carbon (MWAC 1 or MWAC 2) was added into a series of 250 mL conical flasks, containing 100 mL of 10 mg/L of Cr(VI) wastewater. To determine the effects of temperature, four numbers of such flasks were agitated at an arbitrary rotational speed of 130 rpm (as done for kinetic study) in an incubator shaker at different temperatures of 20, 30, 35, and 40 °C, for a period equal to the equilibrium time determined in kinetic experiment. Effluent Cr(VI) concentration was measured after filtration either by AAS or colorimetric method. The temperature at which maximum removal of Cr(VI) was observed was considered as optimum temperature. To determine the effects of agitation speed: three numbers of such conical flasks were agitated at optimum temperature for a period of equilibrium time at different rotational speed of 100, 200, and 300 rpm. The mixture was filtered through Whatman filter paper (No. 40), and Cr(VI) concentration was measured. The agitation speed at which maximum removal of Cr(VI) was observed was considered as optimum agitation speed. To know the effects of pH: the pH of the mixture of four such conical flasks was adjusted to 1.5, 2.0, 4.0 and 6.5 using sulfuric acid and/or sodium hydroxide solution. The flasks were agitated at optimum temperature and optimum agitation speed for a period equal to the equilibrium time. The pH at which maximum Cr(VI) removal was observed is considered as the optimum pH for further study.

2.4. Equilibrium study

Equilibrium study was performed by bottle point isotherm technique as suggested by Sontheimer et al. [37]. 100 mL of 10 mg/L of Cr(VI) containing wastewater were poured into a series of 250 mL conical flasks, containing predetermined amounts of any one of the adsorbents, MWAC 1 or MWAC 2, at a dose of 2 g/L. The equilibrium study was performed under optimum experimental conditions (optimum temperature, optimum agitation speed and optimum pH) for a period of equilibrium time. A blank with same amount of Cr(VI) wastewater but no adsorbent, was subjected to the same procedure to serve as control. After the selected contact time had elapsed, the contents of the bottles were filtered through filter paper (Whatman 40) connected to a filtration assembly, and concentration of chromium was measured.

2.5. Column study

Up-flow fixed bed adsorption columns using modified waste activated carbon, MWAC 2 as adsorbent, was run to evaluate its performance in removing Cr(VI) in continuous mode of operation and determination of constants for bed depth service time (BDST) model [38]. A glass column of 50 cm length and 1 cm internal diameter was used as packed bed adsorption column. Expansion of the adsorption bed was prevented by packing glass wool at inlet and outlet ends of

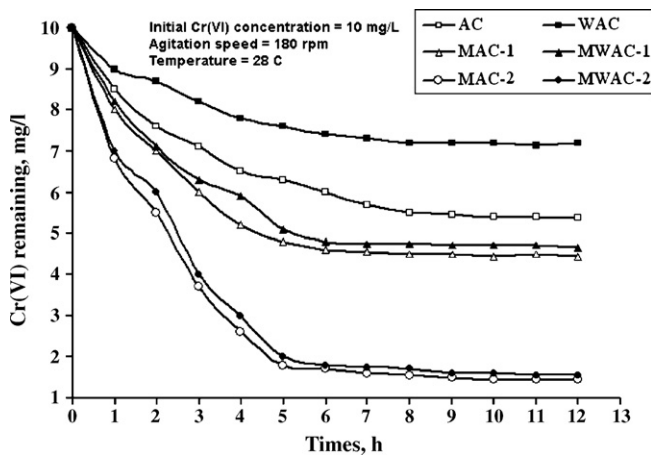


Fig. 1. Kinetic study of various adsorbents.

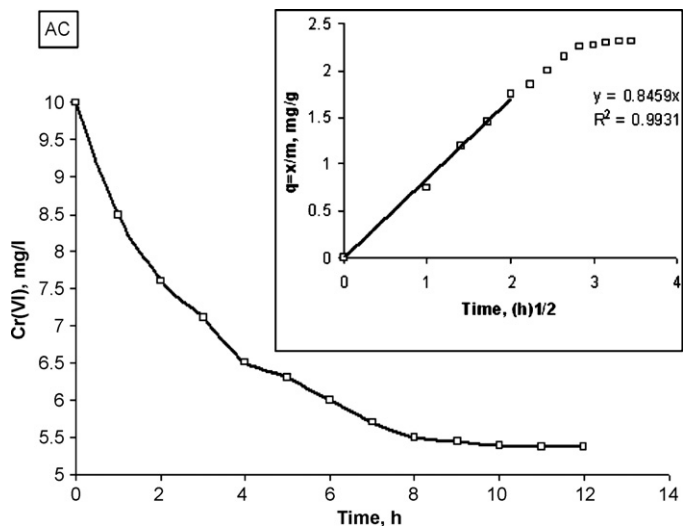


Fig. 2. Rate of adsorption of AC.

the column. Four bed depths of 10, 20, 30 and 40 cm were considered in the present study. Amounts of adsorbent (MWAC 2) taken for three bed depths are 4.6, 9.7, 14.6 and 18.9 g, respectively. The linear flow rate was $0.02 \text{ m}^3/(\text{min m}^2)$. Distilled water spiked with 10 mg/L of Cr(VI) was passed through the adsorption bed from the bottom, at a linear flow rate of $1.2 \text{ m}^3/\text{m}^2 \text{ h}$, using a peristaltic pump (Model: RH-P100VS-100, Chennai, India). When effluent Cr(VI) concentration was more than 90% of influent concentration, the column with bed depth 10 cm was replaced by fresh adsorbent and experiment was restarted with the next higher depth. Experiments with bed depth of 20, 30 and 40 cm were stopped after Cr(VI) concentration in the effluent had reached 0.05 mg/L.

3. Results and discussion

3.1. Kinetic study

For kinetic study of Cr(VI) adsorption, all the 6 grades of adsorbents (Table 1) were considered in the present investigation. The solution pH was adjusted to 2.0 to conduct the adsorption test below the isoelectric point of the carbon used, so that carbon will have a positive charge and would therefore promote the adsorption of the negatively charged chromium species [21]. It is reported that for most of the activated carbons, isoelectric point is near 2.0 and at low concentration the usual form of Cr(VI) near to this pH is HCrO_4^- and CrO_4^{2-} [39]. Furthermore, several researchers observed the maximum removal of Cr(VI) by various adsorbents including activated carbons, at highly acidic solution pH of 1.5–3.0 [21,49–53]. However, based on the performance of all the 6 grades of adsorbents during kinetic study that were conducted at solution pH of 2.0, experiment was conducted to determine the optimum values of temperature, agitation speed and pH of only selected adsorbents. Kinetics of hexavalent chromium adsorption by various grades of adsorbents (Table 1) is given in Fig. 1. Fig. 1 showed that removal of Cr(VI) by acid modified adsorbents was almost ceased within 6 h of agitation period, whereas it took 8 h by AC and WAC to reach to equilibrium. Furthermore, total removals of Cr(VI) by AC and WAC were significantly lower than the other four grades of adsorbents. Removal of Cr(VI) by AC and WAC after 8 h of agitation were 46% (3.16 mg/g) and 27% (2.15 mg/g), respectively; whereas, MAC 1, MWAC 1, MAC 2 and MWAC 2 could remove 54.0% (2.7 mg/g), 52.0% (2.6 mg/g), 83% (4.15 mg/g) and 82% (4.1 mg/g) Cr(VI), respectively, after only 6 h of agitation. Significantly poor performance of WAC (27% removal after 8 h reaction) might be due to its prior use for tap water purification. Better performance of acid treated adsorbents (i.e., MWAC and MAC) than distilled water treated adsorbents

(i.e., WAC and AC) might be due to an increase in acidic functional groups [40] that helps in adsorption of more Cr(VI) ions. Improved Cr(VI) removal by adsorbents due to modification by mineral acids might be due to the formation of positive hydronium ions such as $-\text{COOH}_2^+$, OH_2^+ , and $=\text{C}=\text{OH}^+$ under acidic condition [41–42]. In this study nitric acid modified adsorbents showed better performances than that of sulfuric acid treated AC and WAC. Positive influence of nitric acid at elevated temperature on surface modification of activated carbon on various metal removals has been reported by many researchers [43–45]. Rates of adsorption were measured by determining the change in concentration of the Cr(VI) as a function of time. Graphs were plotted between the amount of Cr(VI) adsorbed per unit weight of adsorbent, $x/m = q$, versus square root of time of contact ($t^{1/2}$) for a contact period, up to which it followed linear trend [46–48]. The rate determined from this method is expressed in terms of $\text{mg/g/h}^{1/2}$. Although this does not represent the true rate, it is useful for comparison [46–48]. Adsorption rate of all the six adsorbents, calculated by plotting graphs as described above, is shown in Figs. 2–7, and the values are given in Table 2.

As observed, performance of MAC 1 and MAC 2 in terms of extent of Cr(VI) removal (Fig. 1) and rate of adsorption (Table 2) were almost same to that of MWAC 1 and MWAC 2, respectively. Being waste products, MWAC 1 and MWAC 2 were selected for

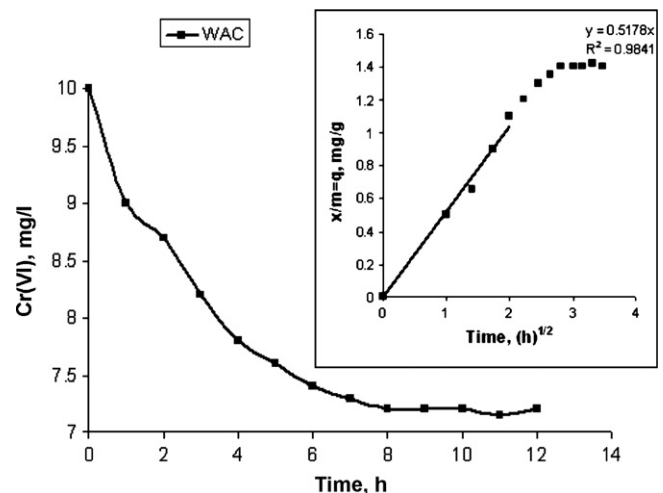


Fig. 3. Rate of adsorption of WAC.

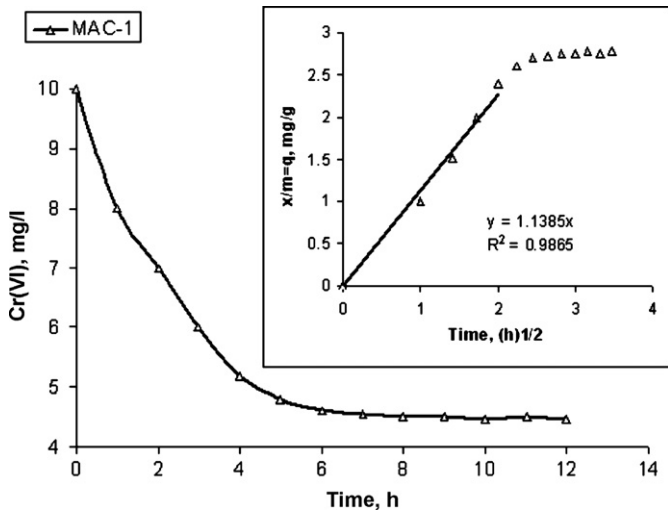


Fig. 4. Rate of adsorption of MAC 1.

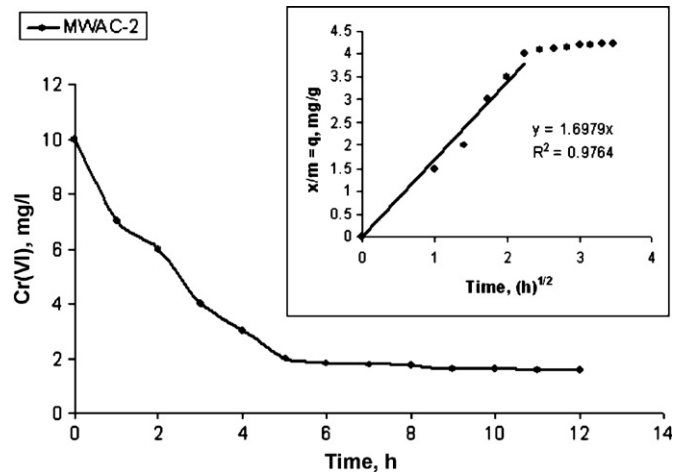


Fig. 7. Rate of adsorption of MWAC 2.

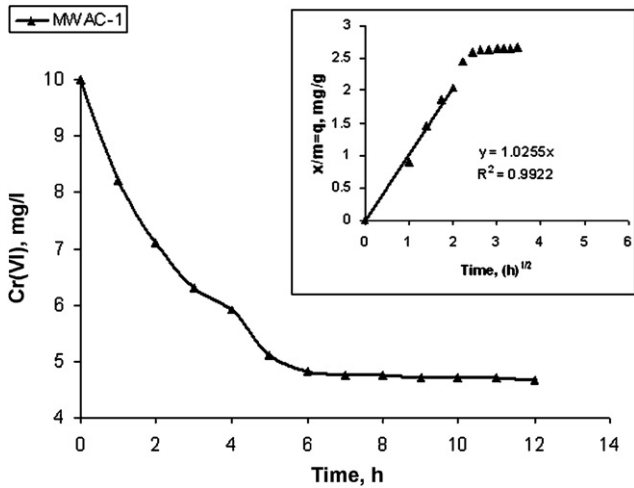


Fig. 5. Rate of adsorption of MWAC 1.

further study. As no significant Cr(VI) removal was observed after 6 h of agitation by the selected adsorbents, 6 h duration is considered as the equilibrium reaction time for further study to determine the optimum agitation speed, optimum temperature, effects of pH

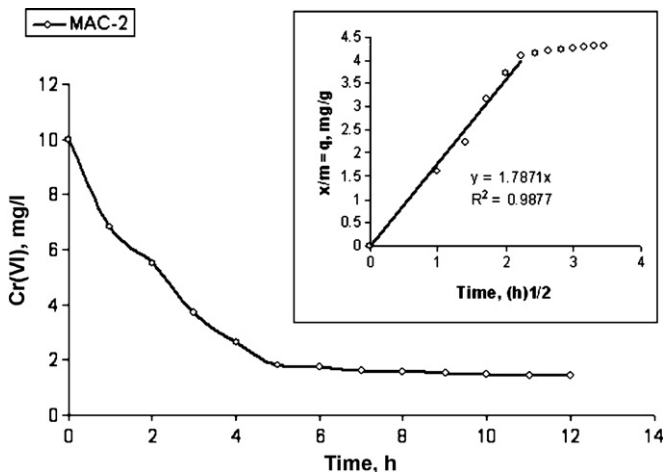


Fig. 6. Rate of adsorption of MAC 2.

Table 2
Adsorption rate on Cr(VI) removal by various grades of adsorbents.

Adsorbent	AC	WAC	MAC 1	MWAC 1	MAC 2	MWAC 2
Adsorption rate (mg/g/h ^{1/2})	0.8459	0.5178	1.1385	1.0255	1.7871	1.6979
Period up to which linear (h)	4	4	4	4	5	5
R ²	0.9931	0.9841	0.9865	0.9922	0.9877	0.9764

and isotherm constants with the above two adsorbents. Optimum temperature determined from the experimental data is 38 °C and the optimum agitation speed is 220 rpm. Hexavalent chromium removal decreased with the increase in pH. Maximum removal of Cr(VI) was observed from highly acidic solutions with pH of 2.0 and 1.5. Similar results were observed by many researchers while studying adsorption of Cr(VI) on various adsorbents (Figs. 8–11) [49–53].

3.2. Equilibrium isotherm study

On the basis of adsorption kinetic study, MWAC 1 and MWAC 2 were selected for equilibrium isotherm study at optimum temperature of 38 °C and agitation speed of 220 rpm. Equilibrium time for the test was 6 h. Equilibrium data were plotted to the following linear forms of Langmuir isotherm and Freundlich isotherm, as given below, to determine the isotherm constants.

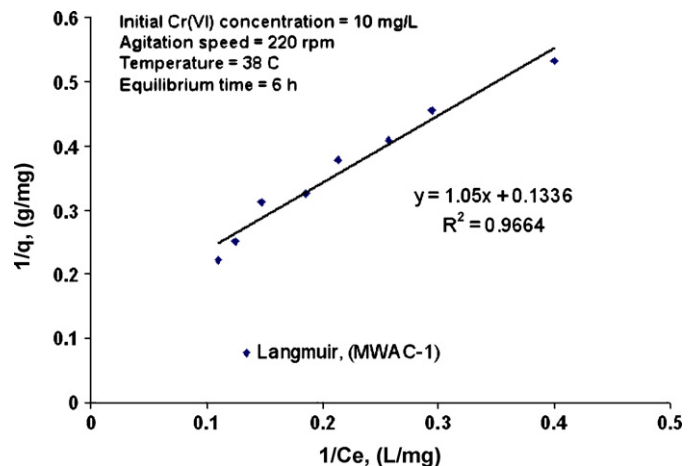


Fig. 8. Linear plot of Langmuir isotherm on Cr(VI) removal by adsorbent MWAC 1.

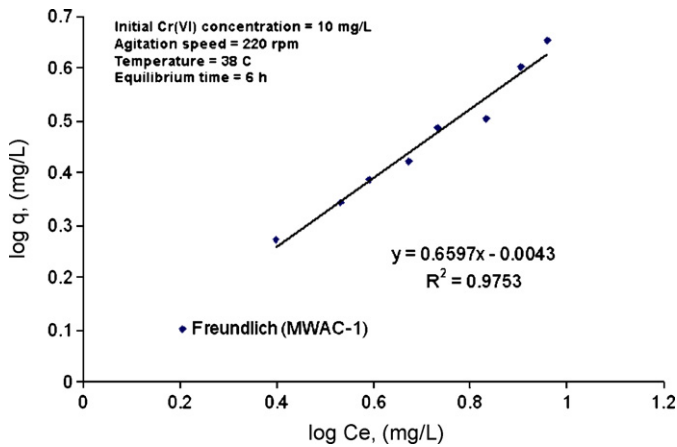


Fig. 9. Linear plot of Freundlich isotherm on Cr(VI) removal by adsorbent MWAC 1.

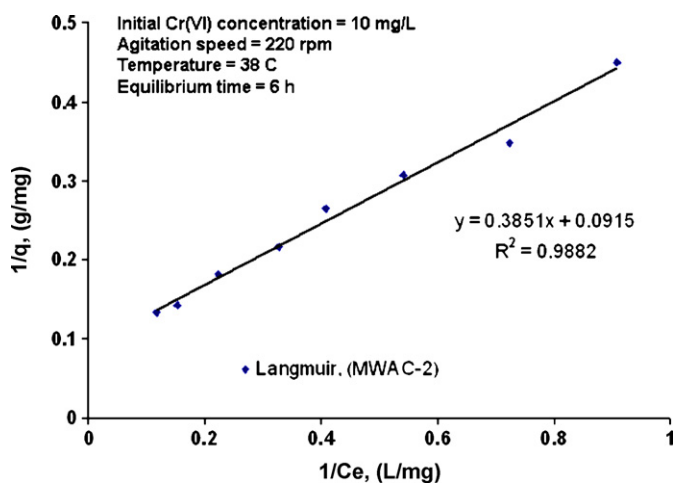


Fig. 10. Linear plot of Langmuir isotherm on Cr(VI) removal by adsorbent MWAC 2.

Linear form of Langmuir isotherm:

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{b \cdot q_{\max}} \cdot \frac{1}{C_e}$$

Linear form of Freundlich isotherm

$$\log q_e = \log K_f + \log C_e$$

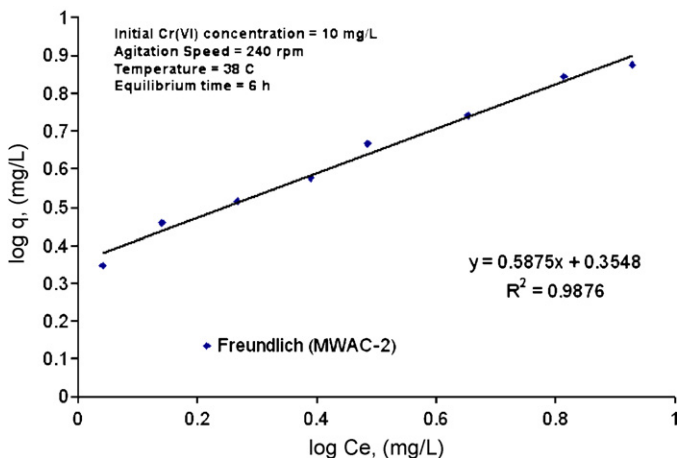


Fig. 11. Linear plot of Freundlich isotherm on Cr(VI) removal by adsorbent MWAC 2.

Table 3
Langmuir and Freundlich isotherm constants.

Adsorbent	Langmuir isotherm constants			Freundlich isotherm constants		
	q_{\max} (mg/g)	b	R^2	K_f (mg/g)	n	R^2
MWAC 1	7.4850	7.859	0.9664	0.9901	1.5158	0.9753
MWAC 2	10.9290	4.2087	0.9882	2.2636	1.7021	0.9876

where, ' q_{\max} ' and ' b ' are the Langmuir isotherm constants; and ' K_f ' and ' n ' are the Freundlich isotherm constants, determined from the slopes and intercepts of the plots shown in Figs. 3–6. The constants thus determined are given in Table 3. Maximum adsorption capacity (q_{\max}) of MWAC 1 and MWAC 2, calculated from Langmuir isotherm plot are 7.485 and 10.929 mg/g, respectively. Liu et al. [34] reported better adsorption capacity by nitric acid modified activated carbon ($q_{\max} = 13.7457$ mg/g) than MWAC 2. This might be due to use of chromium solution with varying concentration of Cr(VI) from 5 to as high as 50 mg/L, while performing equilibrium isotherm study [34]. Higher initial pollutant concentration influence more pollutant to move towards solid phase. In the present study initial concentration of Cr(VI) was kept same (i.e., 10 mg/L) in all the conical flasks. This is to give better representation to a particular strength wastewater. In another report, the maximum adsorption capacity of a fresh activated carbon calculated from Langmuir isotherm was only 3.46 mg/g at an optimum pH of 3.0, where the initial Cr(VI) concentrations in solution were varied between 5 and 20 mg/L [54]. This suggests that suitable modification of waste activated carbons can give better performance than a fresh commercialized activated carbon on Cr(VI) removal from water. Being a waste product, the cost of waste activated carbon is expected to be less than that of a commercialized fresh activated carbon.

3.3. Column study

Equilibrium isotherm study result showed that the maximum adsorption capacity q_{\max} , as calculated from Langmuir isotherm equation, of MWAC 2 is better than that of MWAC 1 (Table 3). Therefore, MWAC 2 was selected for column study to determine the constants of BDST model. The break point considered in the present investigation is the point at which Cr(VI) reaches to appear 0.05 mg/L in the effluent, which is the standards in India for drinking water [16]. Initial concentration of Cr(VI) to the column is 10 mg/L and the linear flow rate is 2 cm/h. The breakthrough curves with the above defined breakpoint for all the four bed depths were drawn between effluent Cr(VI) concentration and throughput vol-

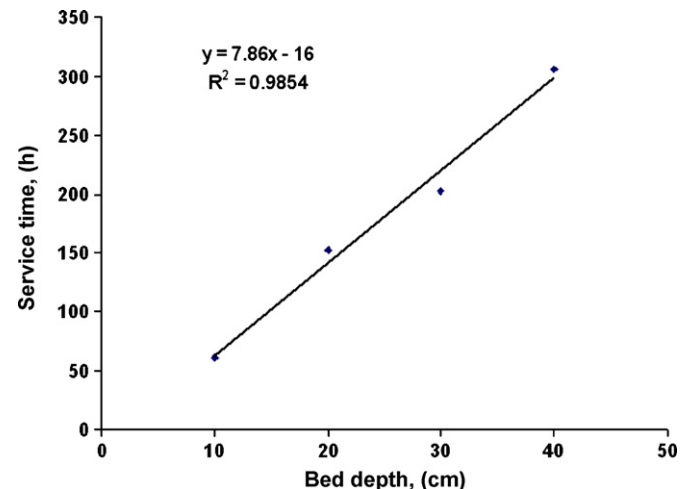


Fig. 12. Bed depth service time plot for MWAC 2.

ume. From the column study results, hexavalent chromium removal capacities of the MWAC 2 were calculated by considering the area under the breakthrough curves for the entire operational periods until the column reached break point [i.e., effluent Cr(VI) concentration = 0.05 mg/L]. Throughout the column run amount of hexavalent chromium removal were 57.45, 143.17, 192.28 and 288.19 mg from 10, 20, 30 and 40 cm bed depths, respectively. The specific Cr(VI) removal capacity of MWAC 2 calculated were 12.49, 14.76, 13.16 and 15.01 mg/g, respectively. A plot between bed depth, d (cm) in X axis, and service time, t (h) in Y axis, followed linear trend (Fig. 12) with slope ('a') = 7.86 (h/cm) and intercept ('c') = -16 h, with $R^2 = 0.9854$. Thus, a useful equation for column design of with BDST approach developed from experimental data is:

$$t = 7.86x - 16$$

where, t = service time (h) and x = bed depth (m).

4. Conclusion

Among the six grades of adsorbents, viz., AC, WAC, MAC 1, MWAC 1, MAC 2, and MWAC 2, acids modified adsorbents showed significantly better degree and rate of removal of Cr(VI) from AC and WAC. Performance of acid modified AC and WAC were found almost equal. Optimum agitation speed, temperature and pH were found to be 220 rpm, 38 °C and 2.0, respectively. Nitric acid modified adsorbent was found with better capacity of Cr(VI) removal than sulfuric acid modified adsorbent. Maximum adsorption capacity (q_{max}) of the selected adsorbents treated with sulfuric acid (MWAC 1) and nitric acid (MWAC 2), calculated from Langmuir isotherm are 7.485 and 10.929 mg/g, respectively. The maximum adsorption capacity of modified waste activated carbons used in the present study were found comparable or even better than that of the fresh activated carbons used by various researchers. Being a waste material, use of waste activated carbon in place of commercialized activated carbons is advantageous in terms of cost of treatment. Experimental data, after adsorption column study, fits well to linear form of BDST model. The equation can be modified to make suitable for a different flow rate and effluent Cr(VI) concentration.

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