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Effect of acid modification on adsorption of hexavalent chromium (Cr(VI)) from aqueous solution by activated carbon and carbon nanotubes

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ABSTRACT

The present study addresses the application of raw and modified carbon nanotubes (CNTs) and activated carbon (AC) for the removal of hexavalent chromium (Cr(VI)) from aqueous solution. Surfaces of both the adsorbents were modified by acid treatment. Nitric acid was used to remove impurities and to introduce carboxylic functional groups on the surfaces of CNTs and AC. Raw and modified adsorbents (CNTs and AC) were characterized by scanning electron microscopy, Brunauer–Emmett–Teller surface area analysis, and thermogravimetric analysis. The influence of adsorbent dosage, contact time, agitation speed, and solution pH were evaluated on the Cr(VI) removal efficiency using batch adsorption experiments. The optimum pH for maximum adsorption of Cr(VI) was found to be 3 and 4 for AC and CNTs, respectively. Modified and raw AC were able to remove 99 and 92% of Cr(VI) ions, respectively, at 75 mg adsorbent dosage, agitation speed of 200 rpm, initial Cr(VI) concentration of 1 mg/L, contact time of 4 h, and solution pH 3, while the removal of Cr(VI) ions recorded maximum values of 87 and 80% for modified and raw CNTs under same treatment conditions. However, acid modification of CNTs was found to have no major effect on the percentage removal of Cr(VI) ions at low adsorbent dosage. Adsorption capacities of both the adsorbents were determined using batch adsorption experiments and experimental data were described by Langmuir and Freundlich adsorption isotherm models. However, Langmuir isotherm model was able to best describe the adsorption of Cr(VI) ions on raw and modified forms of CNTs and AC. Maximum adsorption capacity (q_e) was found to be 2.024 and 1.805 mg/g for raw and modified AC, while 1.021 and 0.964 mg/g for raw and modified CNTs.

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Keywords: Hexavalent chromium; Adsorption; Carbon nanotubes; Activated carbon; Water treatment

1. Introduction

Discovered by French chemist Louis Vauquelin in 1797, chromium is the sixth most abundant transition metal. Chromium is found in natural deposits which contain other elements such as ferric chromite ($FeCr_2O_4$), chrome ochre (Cr_2O_3), and crocoite ($PbCrO_4$) [1,2]. Industrial sources of chromium are wastewater from textile industry, wood preservation, glass industry, dyes and pigments, production of steel and alloys, mining of chrome ore, leather tanning, electroplating, and metal cleaning [2–5].

Chromium is naturally found in different oxidation states including 2+, 3+, and 6+. It can exist in water as dichromate (CrO_4^{2-}) ions, hydrogen chromate ion ($HCrO_4^-$), chromic acid (H_2CrO_4), and chromate ion (CrO_4^{2-}) [6–8]. However, the trivalent Cr(III) and hexavalent Cr(VI) are the most stable forms and most likely to be present in water in neutral pH range. Chromium concentration in industrial water varies from 5.2 to 208,000 mg/L [9,10]. The World Health Organization (WHO) designated a guideline value of 50 μ/L for chromium in drinking water [11–13], while the allowable limit for Cr(VI) in water as suggested by the US Environmental Protection Agency is 0.1 mg/L [12–15].

This stringent limit of chromium in potable water by WHO is due to its severe toxicity to human body. However, Cr(VI) is more toxic (almost 300 times) than Cr(III) due to its mutagenic and carcinogenic nature [16]. Exposure to Cr(VI) may cause repository problems (asthma), internal hemorrhage, dermatitis, kidney and liver damage, dermatitis, and nausea. Skin and eye contact may cause nasal septum, ulceration, irritation, severe burn and permanent damage to eye [17,18].

Various techniques have been employed for the removal of Cr(VI) from water including membrane technologies [19,20], ion exchange [21–24], coagulation, floatation [25], solvent extraction [26], cyanide treatment [27], and adsorption [1,6,7]. In addition to the aforementioned techniques, reduction of Cr(VI) to Cr(III) followed by Cr(III) adsorption on the adsorbent surface has also been reported to be an effective approach for the removal of Cr(VI) ions from water. The reduction is strongly dependent on the pH value and initial Cr(VI) concentration of the solution [12,28,29]. Various materials, such as Fe(II) [30,31], zero-valence Fe [32], zero-valence Al [33], polymers [34,35], and biomass [36,37] can be used for simultaneous adsorption and reduction of Cr(VI) ions to Cr(III) ions [29]. But this process produces an enormous amount of solid waste, which cannot be separated and recycled easily. Ion exchange is another useful technique; however, this process is not economical due to high operational costs.

Nowadays, adsorption is the most widely used and versatile method for removal of various contaminates from water. Different adsorbents are used for the removal of chromium ions from water. The removal of chromium using bacteria, algae, fungi, and different plants has been reported in literature; but, the results though good on lab scale, the poor natural abundance of these materials is a big hurdle in implementation of these methods on large scale [38].

Since their discovery in 1991, carbon nanotubes (CNTs) have gained considerable attention due to their chemically stable nature, large specific area, and excellent mechanical and electrical properties [39]. Water purification using CNTs as an adsorbent has been reported by many researchers. CNTs have been employed for the removal of metal ions, including copper, silver, lead, and nickel [40]. The unique structural properties of CNTs have made them an excellent adsorbent material for the removal of various contaminants from water. The modification of CNTs improves their removal efficiencies for various contaminants [41].

Activated carbon (AC) has also been widely employed for the removal of a number of pollutants from water. The main sources of AC are bagasse ash, wood, agricultural waste, and coconut shells [42,43]. Both granular-activated carbon and powder-activated carbon (PAC) can be employed for water purification. The various contaminants that have been removed from water using AC include lead [42,43], chromium [44], copper [45], cyanide [46], organic matter, and turbidity [47].

In this work, raw and modified forms of CNTs and AC were used for the removal of Cr(VI) from aqueous solution. Acid treatment was used for surface modification of these adsorbents by producing carboxylic groups on their surfaces. The aim was to compare the removal efficiencies of modified and raw adsorbents and determine the optimum parameters for maximum removal of chromium (VI). The raw and modified adsorbents were characterized by scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) surface area analysis, and thermogravimetric analysis (TGA). The effect of different parameters i.e. dosage of the adsorbent, contact time, agitation speed, and pH of the solution were investigated on the removal of Cr(VI) from water. The adsorption experimental data were represented by both the Langmuir and Freundlich isotherm models.

2. Experimental

2.1. Carbon-based adsorbents

CNTs were obtained from Nanostructured & Amorphous Materials, Inc., USA. The specifications of CNTs are shown in Table 1. The activated carbon was obtained from Calgon, in 10–30 mesh (0.60–1.0 mm) size. The granular-activated carbon was milled in a hammer-cutter mill to a powder (<0.18 mm in particle diameter). The surface area of the PAC was measured by N_2 adsorption at 77 K using a 15-point BET technique on the analysis port of analyzer (Micromeritics, Norcross, GA). The chemical and physical properties of the activated carbon are shown in Table 2. The values of BET surface area for raw and modified CNTs and AC are presented in Table 3.

2.2. Oxidation of the carbon-based adsorbents

Initially, 2 g of each adsorbent (CNTs and AC) was added to 300 ml of a concentrated (69%) nitric acid solution. The resulting suspensions were heated to 80˚C and refluxed for 48 h at 120˚C. The mixture was cooled to room temperature and diluted using 500 mL of deionized water to remove free oxidants and to attain a constant pH. The mixture was vacuum filtered using Whatman Grade 42 filter paper (2.5 μm pore size). The oxidized adsorbents were dried at 100˚C using a vacuum oven.

Acid treatment is expected to open the tube caps and reduce the length of CNTs [48,49]. Both CNTs and AC were modified in similar ways and the process resulted in the attachment of functional groups (mainly carboxylic) at different adsorption sites on the surfaces of both the adsorbents. The oxidation of carbon adsorbents removes impurities from the surface and makes the surface more hydrophilic [50,51].

Table 1
Chemical and physical properties of the CNTs

Property	Value
Outer diameter (nm)	10–20
Length (um)	1–10
Purity	>95%
Ash	<1.5 weight%
Specific surface area (m^2/g)	156
Electrical conductivity (s/cm)	>10^2

Table 2
Chemical and physical properties of the activated carbon

Property	Value
Surface area (m^2/g)	1,126
Bulk density (g/cm^3)	0.44 ± 0.003
Ash content (%)	8.3 ± 0.8
pH	7.9 ± 0.5
Attrition (%)	10.8 ± 3.2
Conductivity (μS)	4.7 ± 2.8

Table 3
BET surface area of raw and modified adsorbents

Adsorbent	BET surface area (m^2/g)
Activated carbon	1,126
Modified activated carbon	1,420
Carbon nanotubes	156
Modified CNTs	170

The amounts of carboxylic groups on the surfaces of both the adsorbents were quantitatively measured using Boehm's method [52]. In this method, 0.3 g of adsorbent was dispersed in 100 mL of deionized water. The resultant suspensions were then mixed with 10 mL of 0.1 M NaOH, $NaHCO_3$, and Na_2CO_3 and stirred in a sealed vessel for 24 h. Then the suspensions were filtered, and 25 mL of filtrate was added to 20 mL of 0.1 M HCl. The solution was back titrated with 0.1 M NaOH, and the volume of NaOH needed to neutralize the pH of the solution to 7 was measured. Amount of carboxyl groups on the surfaces of CNTs and AC were 0.52 and 0.76 mmol/g, respectively.

2.3. Characterization of the adsorbents

Various analytical techniques were used to observe the surface characteristics of the raw and modified adsorbents. TGA was performed using thermogravimetric analyzer (K.U. Leuven SDT, Q600) at a heating rate of 10˚C/min in air. The surface areas of the adsorbents were measured using a surface area analyzer (Micromeritics, Norcross, GA) with a 15-point BET and Nitrogen adsorption at 77 K. The Boehm's titration method was employed to measure the amount of functional groups on the adsorbent's surfaces (CNTs and AC). SEM studies were performed using field emission scanning electron microscope (TESCAN MIRA 3 FEG-SEM).

2.4. Batch mode adsorption experiment

To study effects of the variables on the adsorption of Cr(VI) ions by CNTs and AC, batch experiments were performed at ambient temperature. In these experiments, the effects of adsorbent dosage, pH of the initial solution, agitation speed, and contact time were studied on the adsorption of Cr(VI) ions. Inductively coupled plasma mass spectrometer (X-Series 2 Q-ICP-MS) was employed to measure the concentration of Cr(VI) before and after the experiment.

The equilibrium adsorption capacity was calculated using the following equations:

$$\text{Percentage removal} = \frac{C_i - C_e}{C_i} \times 100 \tag{1}$$

$$\text{Adsorption capacity, } q_e \text{ (mg/g)} = \frac{C_i - C_e}{M} \times V \tag{2}$$

where C_i and C_e are the initial and equilibrium concentration (mg/L) of Cr(VI) ions, q_e (mg/g) is the equilibrium adsorption capacity, M (g) is the weight of the adsorbent, and V (L) is the volume.

2.5. Preparing the stock solution

A solution of 1 mg/L of Cr(VI) was prepared for the analysis. Initially, all of the impurities on the glassware were removed by washing with 2% nitric acid. Washing the glassware not only removes the contaminants from the wall, but also prevents further adsorption of chromium ions. A standard solution of Cr(VI) (1,000 mg/L) was used to produce the stock solution. Two milliliters of Cr(VI) was added to a 2 L volumetric flask, followed by deionized water to reach a total volume of 2 L. A magnetic stirrer was used for uniform mixing of the solution. For pH adjustment of the stock solution, 1.0 M NaOH and 1.0 M HNO_3 were used. A constant pH was maintained by the addition of buffer solution.

2.6. Adsorption isotherms models

Adsorption of Cr(VI) ions on the adsorbents were analyzed using the Freundlich and Langmuir isotherm models.

The Freundlich isotherm can be represented by the equation:

$$Q_e = K_F\, C_e^{1/n} \tag{3}$$

where C_e is the adsorbate concentration (mg/L), Q_e is the adsorption density, and n and K_F are empirical constants that are dependent on several environmental factors. The linear form of the above equation is expressed as:

$$\ln Q_e = \ln K_F + 1/n \ln C_e \tag{4}$$

A straight line can be obtained by plotting ln [C_e] vs. ln [Q_e]. If the data are fitted well by the Freundlich isotherm model, the empirical constants can be determined from the intercept and the slope.

The Langmuir adsorption isotherm is given by the equation:

$$Q_e = X_m K C_e/(1 + K C_e) \tag{5}$$

where C_e is the concentration of adsorbate in solution (mg/g), Q_e is the adsorption density at the equilibrium solution concentration C_e, K is the Langmuir constant, and X_m is the maximum adsorption capacity (mass of solute adsorbed/mass of adsorbent). Rearrangement of the above equation yields:

$$C_e/Q_e = 1/X_m K + C_e/X_m \tag{6}$$

The experimental data can be represented by this linear form of the equation by plotting C_e/Q_e vs. C_e. Based on the intercept and slope of the plot, the Langmuir constants K and X_m can be evaluated, respectively.

2.7. Kinetic modeling

The adsorption of Cr(VI) by CNTs and AC were analyzed using pseudo-first-order, second-order and pseudo-second-order rate equations, as shown below:

Pseudo-first-order

$$\log\,(q_e - q_t)/q_e = -K_L\, t/2.303 \tag{7}$$

Second-order

$$1/(q_e - q_t) = 1/q_e + kt \tag{8}$$

Pseudo-second-order

$$t/q_t = 1/\left(2K_s q_e^2\right) + t/q_e \tag{9}$$

where K_L is the pseudo-first-order rate constant of adsorption (1/min), q_t is the sorption capacity at time t (mg/g), q_e is the sorption capacity at equilibrium, t is the time (min), and K_s and k (g mg^{-1} min^{-1}) are the pseudo-second-order and second-order sorption rate constants, respectively.

The constants in the above equations (K_L, K_s, and k) can be determined from the slopes of the linear plots of log $(q_e - q_t)$ against t, t/q_t against t, and $1/(q_e - q_t)$ against t, while q_e can be determined from the intercept data for the pseudo-second-order and second-order rate equations.

3. Results and discussion

3.1. Characterization of carbon-based adsorbents

Surface morphologies of the raw and modified adsorbents were observed using FE-SEM. Modification of CNTs has reduced the lengths of CNTs, as shown in Fig. 1. It can also be seen that the confined space in the CNTs has reduced after oxidation**.** Modification of the activated carbon had a visual impact on surface morphology. Fig. 2(a) shows that most of the pores on the AC surface were blocked; however, acid treatment caused opening of some of the blocked pores (Fig. 2(b)). Acid treatment lead to increase in surface area of AC and hence its adsorption characteristics for Cr(VI) removal has increased.

The purity of raw and modified adsorbents was measured using TGA and derivative thermogravimetric analysis (DTGA). The analysis was performed under air and a heating rate of 10˚C/min was maintained during the analysis. The results of the analysis are shown in Fig. 3. TGA reveals that the raw CNTs are stable (Fig. 3(a)), while the modified CNTs (M-CNTs) decompose at relatively lower temperature. This result is expected due to the presence of thermally unstable functional groups. For the modified AC (M-AC), apparently, there were volatile materials that were burned out during the initial heating process, and impurities remained after the heating process. Furthermore, a single peak appeared in the DTGA curve, indicating that amorphous carbon and other impurities from the AC surface were removed by the oxidation process, leaving behind pure material (Fig. 3(b)).

3.2. Effect of pH

Solution pH is one of the critical parameters affecting the adsorption process. The effect of pH on removal of Cr(VI) by raw and modified CNTs and AC is shown in Fig. 4. The value of pH was varied from 2 to 8, while the other variables including contact time, adsorbent dosage, Cr(VI) initial concentration, and agitation speed were kept constant at 4 h, 50 mg, 1 mg/L, and 200 rpm, respectively. Both raw and modified AC showed maximum adsorption of Cr(VI) at pH 3. However, for raw and modified CNTs, the maximum adsorption occurs at pH 4 and 3, respectively.

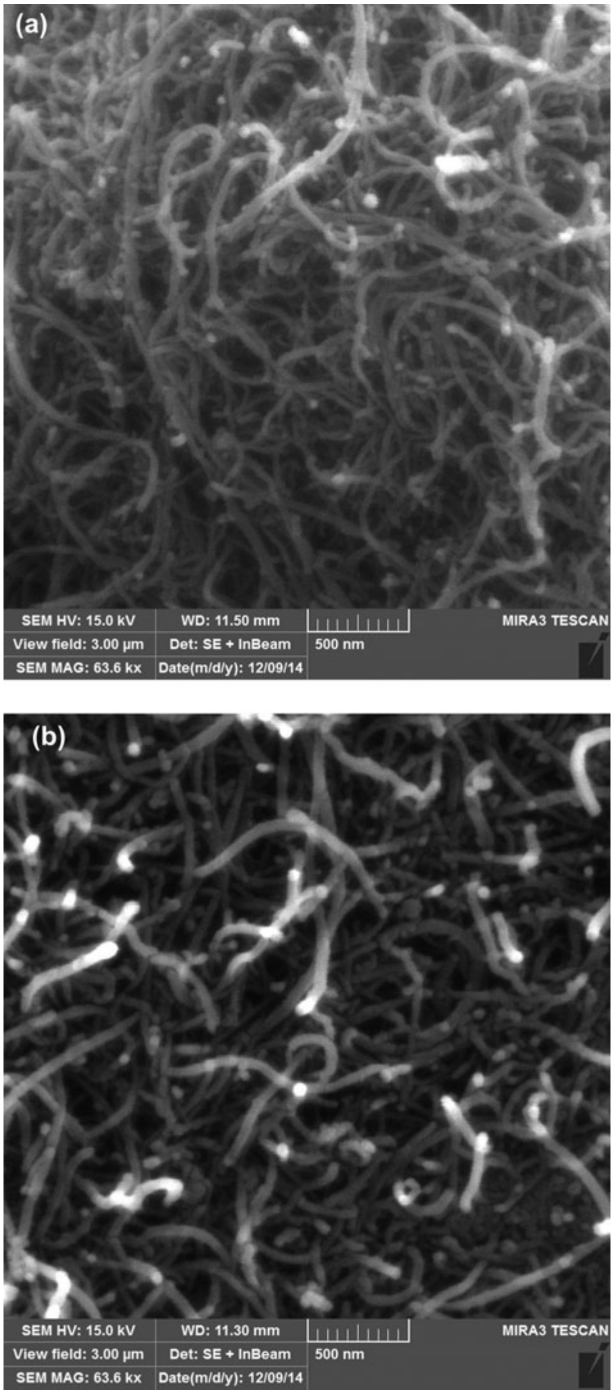


Fig. 1. SEM images of (a) raw CNTs and (b) modified CNTs.

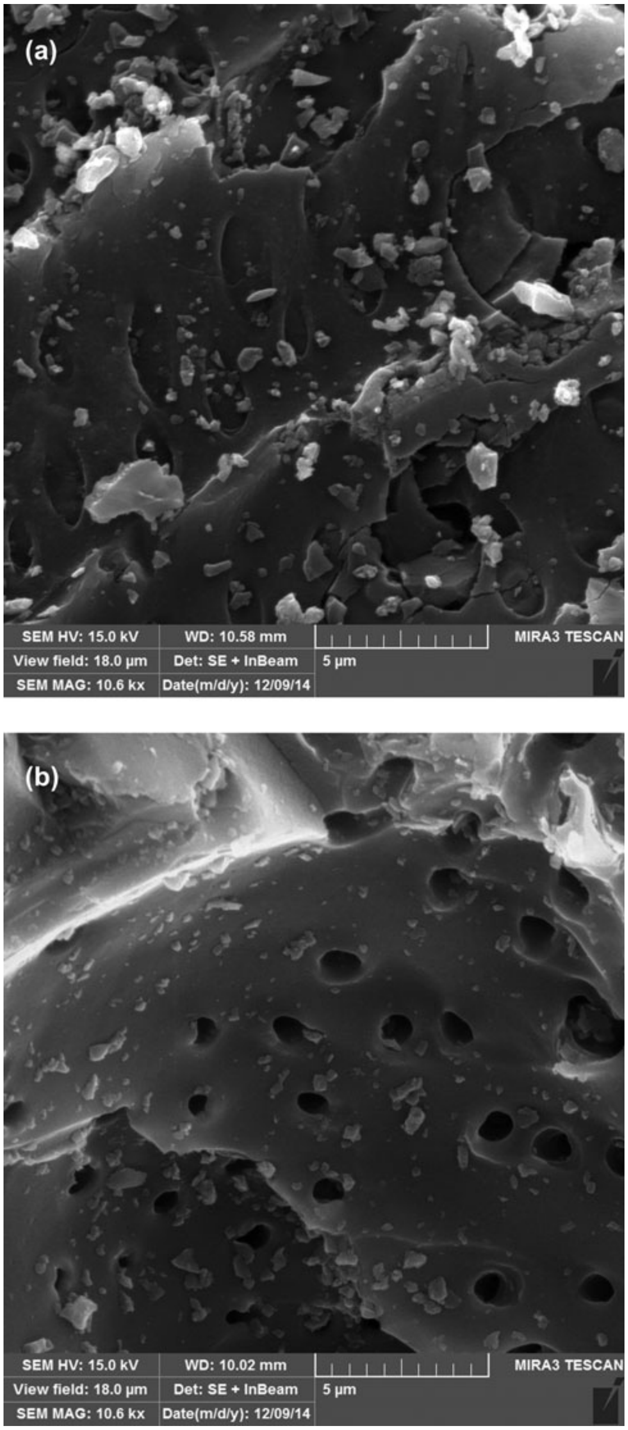
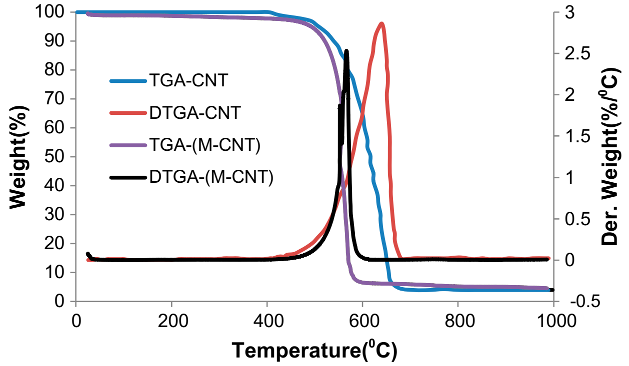
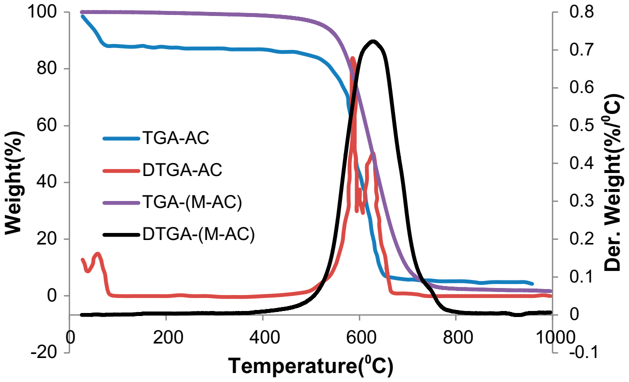


Fig. 2. SEM images of (a) raw AC and (b) modified AC.



(a) CNTs



(b) AC

Fig. 3. TGA and DTGA curves for raw and modified (a) CNTs and (b) AC.

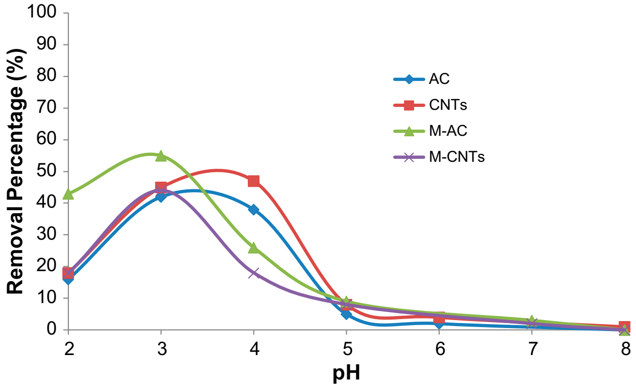


Fig. 4. The effect of pH on percentage removal of Cr(VI).

The effect of pH on adsorption of Cr(VI) ions can be explained on the basis of ionic chemistry of the solution and surface charge of the adsorbents. Depending upon the chromate concentration and solution pH, Cr(VI) may exist in different ionic states including hydrogen chromate ($HCrO_4^-$), dichromate (CrO_7^{2-}), and chromate (CrO_4^{2-}). The equilibrium between the chromate (CrO_4^{2-}) and dichromate ions ($Cr_2O_7^{2-}$) in aqueous solution is shown by the reaction (Eq. (10)) [15,28].

$$2CrO_4^{2-} + 2H^+ \leftrightarrow Cr_2O_7^{2-} + H_2O \tag{10}$$

Dichromate ions ($Cr_2O_7^{2-}$) are the dominant species at lower pH, while at higher pH, only chromate (CrO_4^{2-}) ion exists in the solution. At lower pH, the dominant species $Cr_2O_7^{2-}$ is converted to $HCrO_4^-$, which can be easily turned to Cr(III) ions due to high redox potential (1.33V), as shown by Eqs. (11) and (12) [29,53].

$$Cr_2O_7^{2-} + H_2O \leftrightarrow 2HCrO_4^- \tag{11}$$

$$HCrO_4^- + 7H^+ + 3e \rightarrow Cr(III) + H_2O \quad E_o = 1.33\ V \tag{12}$$

However, at higher pH, the dominant species chromate (CrO_4^{2-}) is converted to a precipitate of $Cr(OH)_3$ due to low redox potential (−0.13 V), as shown in Eq. (13) [15,29,30]:

$$Cr_2O_7^{2-} + H_2O + 3e \rightarrow Cr(III) + 5OH^- \quad E_o = -0.13\ V \tag{13}$$

From Fig. 5, it can be seen that the removal efficiency of Cr(VI) for raw and modified CNTs and AC is higher at lower pH than at higher pH values. This can be explained on the basis of the positively charged surface of the adsorbents at lower pH. The electrostatic interaction between the positively charged adsorbents surface and $Cr_2O_7^{2-}$ anions is responsible for higher removal efficiency of Cr(VI) at lower pH. However, at higher pH, the Cr(VI) removal efficiency is lower due to competition between the chromate (CrO_4^{2-}) and OH^- ions, to cover the limited adsorption sites. Furthermore, surfaces of the adsorbents carry more negative charge, which leads to repulsion between the adsorbent surface and CrO_4^{2-} ions.

It can also be concluded that AC modification has enhanced its removal efficiency and maximum removal of 55% occurs at pH 3, which was higher than the maximum value of 44% at same pH for the raw AC. This might be due to increase in surface area and presence of more active adsorption sites on AC surface after acid treatment. Furthermore, as shown by Boehm's titration results, the amount of functional groups on AC surface is higher than CNTs, which enhanced the adsorption of Cr(VI) ions. However, at higher pH, both the modified and raw AC shows lower removal efficiency for Cr(VI). This can be justified by the fact that precipitation of $Cr(OH)_3$ occurred at higher pH, that reduced the adsorption capacity of the adsorbent.

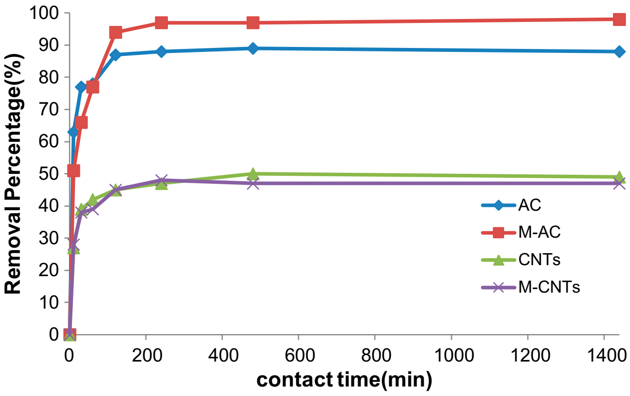


Fig. 5. The effect of contact time on the percentage removal of Cr(VI).

For CNTs, acid modification has no major effect on removal efficiency of Cr(VI). The maximum removal of Cr(VI) for modified and raw CNTs is 44 and 45% at pH 3. This may be attributed to the attachment of negatively charged functional groups to the CNT surface during acid treatment. Therefore, electrostatic repulsions between the CNT surface and chromium anions will decrease the adsorption of Cr(VI). This phenomenon will be more dominant at lower pH, where more negative ions will be present in the solution. It can also be observed that acid treatment brings about very small change in the surface area of CNTs. Therefore, the number of adsorption sites is almost same for both raw and modified CNTs.

3.3. Effect of contact time

In order to study the effect of contact time and to determine the equilibrium time for maximum uptake of Cr(VI) ions by CNTs and AC, experiments were performed over different contact times ranging from 0 to 24 h. All the other parameters including agitation speed, adsorbent dosage initial concentration of Cr (VI), and solution pH were kept constant at 200 rpm, 50 mg, 1 mg/L and 3, respectively.

It is shown in Fig. 5 that Cr(VI) removal by using both raw and modified AC increases with increase in contact time till 4 h. This observation was attributed to the adsorption equilibrium phenomenon, whereby the rate of adsorption was higher than the rate of desorption up to 4 h of contact time, which is the equilibrium adsorption point. At this time, the rate of adsorption and desorption were same and no further removal of Cr(VI) from the solution was achieved. The percentage removal of Cr(VI) after contact time of 4 h was 88 and 98% by raw and modified AC, respectively. The higher adsorption of Cr(VI) ions by modified AC may be due to higher surface area and increase in number of adsorption sites after acid modification.

It can also be observed that the equilibrium time required for removal of Cr(VI) by using modified

CNTs was 2 h; however, Cr(VI) removal continue to increase with increase in contact time till 8 h for raw CNTs. Furthermore, CNT modification has no major effect on removal of Cr(VI) and adsorption capacity is almost same for both raw and modified CNTs. However, for contact time above 4 h, percentage removal by raw CNTs is higher than modified CNTs, and acid treatment of CNTs was not suggested for Cr(VI) removal. This phenomenon can be explained on the basis of surface charge of CNTs after acid modification. Acid modification of CNTs introduces oxygen-containing functional groups and Cr(VI) adoptions are limited due to repulsion between the Cr(V) anions and negatively charged CNT surface.

3.4. Effect of adsorbent dosage

To investigate the effect of adsorbent dosage, batch adsorption experiments were conducted with different doses of adsorbents (CNTs and AC) ranging from 25 to 250 mg, while keeping agitation speed, initial concentration of Cr(VI), contact time, and solution pH constant at 200 rpm, 1 mg/L, 4 h and 3, respectively.

It can be observed from Fig. 6 that removal efficiency of both raw and modified AC increases with increase in adsorbent dosage up to 75 mg. However, no further increase in percentage removal was observed beyond 75 mg of dosage. This indicated the saturation value of AC for removal of Cr(VI) ions. Modified AC was able to remove 99% of Cr(VI) at 75 mg of dosage. However, raw AC could only take about 92% Cr(VI) ions as its maximum removal at optimum dosage of 75 mg. Increase in removal efficiency with increase in adsorbent dosage can be justified due to increase in number of active adsorption sites at higher adsorbent dosage.

For raw and modified CNTs, removal of Cr(VI) ions increases with increase in dosage up to 175 mg and then become constant for the rest of adsorbent dosage range. Raw CNTs removed 80% of Cr(VI) ions at 150 mg dosage and above, while for modified CNTs, percentage removal of 87% was achieved above 175 mg of dosage. Although the parentage behavior by both raw and modified CNTs was almost similar at lower adsorbent dosage, acid treatment may be able to enhance the percentage removal by CNTs, but at higher dosage rate. This increase in removal of Cr(VI) ions at higher adsorbent dosage might be due to the fact that at higher adsorption dosage, the number of active adsorption sites on CNT surface is more. This increase in number of active sites is not only due to acid treatment, but also due to higher amount of CNTs present in the solution.

3.5. Effect of agitation speed

Agitation facilities contact between ions in the solution and adsorbent binding sites and thereby promote effective diffusion of ions toward the adsorbent surface. Experimental runs measuring the effect of agitation speed on the adsorption capacity of Cr(VI) by CNTs and AC are shown in Fig. 7.

The agitation speed was varied from 50 to 250 rpm, while all the other parameters including contact time, adsorbent dosage, initial concentration, and solution pH were kept constant at 4 h, 50 mg, 1 mg/L, and 3, respectively. Results showed that the removal efficiency of Cr(VI) by raw and modified AC increases with increase in agitation speed and maximum removal was achieved at 200 rpm. This can be justified by the fact that effective transport of Cr(VI) ions toward the adsorbent surface occurred due to less resistance to diffusion

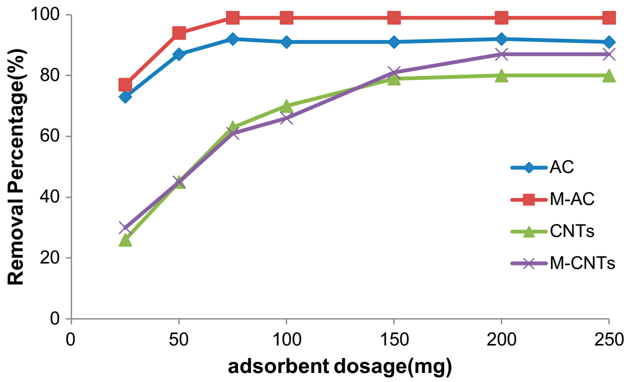


Fig. 6. The effect of adsorbent dosage on the percentage removal of Cr(VI).

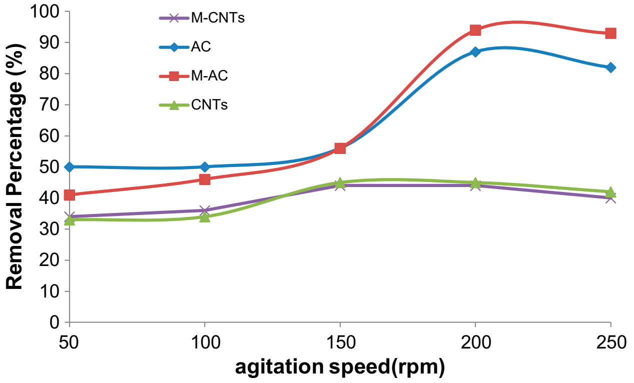


Fig. 7. Effect of agitation speed on the percentage removal of Cr(VI).

at higher agitation speed. However, modified AC has higher removal (95%) than raw AC (85%) at an agitation speed of 200 rpm. Surface modification of AC has enhanced the number of active adsorption sites; therefore, more Cr(VI) ions were adsorbed to modified AC surface as compared to raw AC.

For raw and modified CNTs, removal of Cr(VI) ions increases with increase in agitation speed till 150 rpm at which maximum removal was achieved. However, agitation speed of 200 rpm was used in the rest of the experiments to compare the behavior of AC and CNTs under similar conditions.

It can be seen that no significant change occurs with agitation speed by using raw and modified CNTs. This might be due to the fact that although acid treatment has introduced the functional groups on CNT surface, which provides more adsorption sites, the repulsion between modified CNT surface and Cr(VI) anions counterbalance this effect. Therefore, both raw and modified CNTs showed almost same removal efficiency at similar agitation speed.

3.6. *Langmuir and Freundlich adsorption isotherm models for Cr(VI)*

Equilibrium adsorption data was used to determine maximum capacity of the raw and modified CNTs and AC. Both Langmuir and Freundlich models were employed to describe the data for adsorption of Cr(VI) by these adsorbents. The adsorption intensities and adsorption capacities (q_e) were determined, from the intercept and slope data, respectively, for each adsorbent. Figs. 8 and 9 show Langmuir and Freundlich adsorption isotherm models for Cr(VI), respectively.

It can be seen that Langmuir isotherm shows a good fit model for both raw and modified CNTs; but, for the raw activated carbon, Freundlich isotherm provides much better fit. However, the Langmuir isotherm model application for raw AC is still within the acceptable range ($R^2 > 0.9$); therefore, the Langmuir isotherm model was employed to describe the adsorption of Cr(VI) ions on the surface of all the adsorbents.

From Table 4, it can be seen that the modified AC has much higher adsorption capacity for Cr(VI) ions than raw AC. This might be due to higher surface area and presence of more active sites on AC surface after acid treatment. From the analysis above, it can be concluded that modified AC should be selected for Cr(VI) removal from solutions of low initial concentrations.

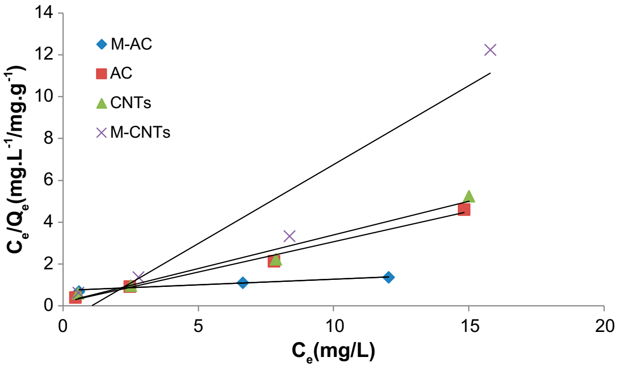


Fig. 8. Langmuir adsorption model for Cr(VI).

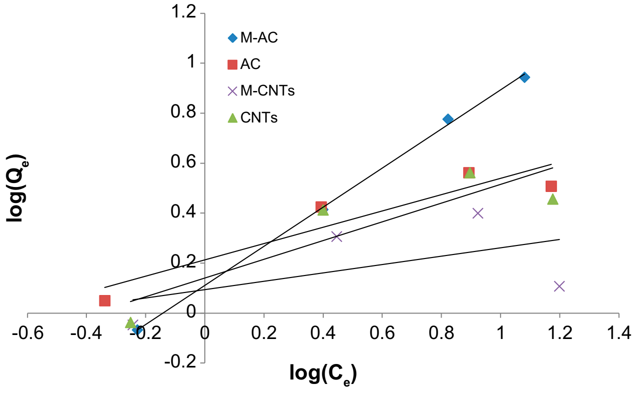


Fig. 9. Freundlich adsorption model for Cr(VI).

Table 4
Parameters of Langmuir and Freundlich adsorption isotherm models for Cr(VI)

	Langmuir			Freundlich		
	q_m	K_L	R^2	N	K_F	R^2
Raw CNTs	3.115	1.773	0.973	2.008	0.791	0.786
Modified CNTs	1.314	−0.929	0.918	5.988	1.099	0.278
Modified AC	18.519	0.073	0.940	1.279	1.117	0.998
Raw AC	3.460	1.690	0.988	4.695	2.462	0.870

Table 5
Correlation coefficients for kinetic models of Cr(VI) adsorption

Adsorbent (50 mg)	1st order	Pseudo 2nd order	2nd order
Raw CNTs	0.306	0.999	0.559
Modified CNTs	0.496	0.999	0.766
Raw AC	0.974	0.999	0.812
Modified AC	0.001	0.994	0.027

Acid treatment has no major effect on the adsorption capacity of CNTs. Both modified and raw CNTs have relatively comparable adsorption capacities ($q_e \approx 1$ mg/g). This is due to the fact that there is a small change in surface area of CNTs after acid modification. The acid treatment has introduced more adsorption sites on the CNT surface, which was expected to enhance the adsorption. But, the introduced carboxylic functional groups might also be involved in a repulsion effect caused by the negative charges of the carboxylic group and the negative charges carried by hydrogen chromate ions ($HCrO_4^-$).

3.7. Kinetics modeling

The kinetic data for adsorption provides a comparison of the performance of different adsorbents under different operational conditions. The data obtained can be used for optimizing process parameters for the removal of pollutants from water. Table 4 shows the correlation coefficients for three models used to describe the behavior of raw and modified CNTs and AC. As per Table 5, the correlation coefficient (R^2) of pseudo-second-order kinetic equation is higher than the other two kinetic equations. Therefore, pseudo-second-order kinetic equation can be used to best describe Cr(VI) ion adsorption by raw and modified CNTs and AC. Hence, for investigating the adsorption of Cr(VI), the pseudo-second-order equation was employed, as shown in Eq. (14),

$$1/q_t = 1/k_2 q_e^2 + t/q_e \tag{14}$$

where q_e and q_t are the sorption capacity (mg/g) at equilibrium and at time (t), respectively. K_2 is the pseudo-second-order rate constant (g mg^{-1} min^{-1}) and h (g mg^{-1} min^{-1}) can be regarded as the initial sorption rate.

The above equation in integrated form is expressed as:

$$t/q_t = 1/h + (1/q_e)/t \tag{15}$$

A linear plot of t/q_t vs. t was obtained and the values of k_2 and q_e were determined from the intercept and slope, respectively.

3.8. Kinetics adsorption model of chromium (VI)

The parameters of kinetics adsorption model for Cr (VI) are shown in Table 4. A plot t/q_t vs. time yields a very good straight line for all the adsorbents, as shown in Fig. 10. From Table 6, it can be concluded that the value of rate constant k_2 is lowest for modified AC and highest for modified CNTs. It can also be observed that value of the equilibrium adsorption capacity (q_e) of the adsorbents follow a descending order: M-AC > AC > CNTs > M-CNTs. Adsorption capacity of modified AC is higher than raw AC, which might be due to

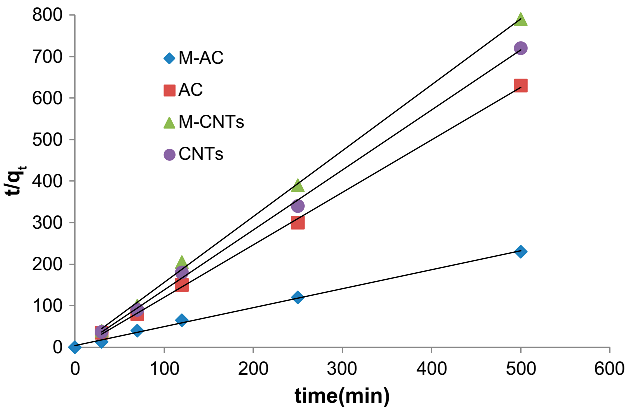


Fig. 10. Pseudo-second-order kinetics for the adsorption of Cr(VI) onto raw and modified CNTs and AC.

Table 6
Kinetic parameters for pseudo-second-order model of Cr (VI)

Adsorbent (50 mg)	q_e (mg/g)	K_2 (g mg^{-1} h^{-1})	R^2
Raw CNTs	1.021	0.035	0.999
Modified CNTs	0.964	0.059	0.999
Raw AC	1.805	0.044	0.999
Modified AC	2.024	0.011	0.994

increased surface area of AC after acid modification. However, modified CNTs have almost same adsorption capacity as the raw CNTs. This implies that the acid modification of CNTs has no major effect on Cr (VI) removal efficiency.

4. Conclusion

Modified and raw CNTs and activated carbon were found to be effective adsorbents for Cr(VI) removal from aqueous solution. The characterization of Cr(VI) uptake showed that the chromium ion binding is dependent on amount of dosage, agitation speed, initial pH, and contact time. The oxidation treatment of adsorbents through the addition of carboxylic functional groups was found to have no major effect on the removal efficiency of Cr(VI) by CNTs. The pH for maximum removal of Cr(VI) was found to be 3 and 4 for AC and CNTs, respectively. Modified and raw AC were able to remove 99 and 92% of Cr(VI) ions, respectively, at 75 mg adsorbent dosage, agitation speed of 200 rpm, initial Cr(VI) concentration of 1 mg/L, contact time of 4 h, and solution pH 3, while the removal of Cr(VI) ions recorded maximum values of 87 and 80% for modified and raw CNTs under same treatment conditions. However, acid modification of CNTs was found to have no major effect on the percentage removal of Cr(VI) ions at low adsorbent dosage. While CNTs and M-CNTs show no major change in the percentage uptake with an increase in the agitation speed from 50 to 250 rpm, AC and M-AC show significant improvement in Cr(VI) removal at 200 rpm. Modified AC showed a higher removal of 94% as compared to regular AC, which has 87% removal at 200 rpm. Adsorption capacities of both the adsorbents were determined using batch adsorption experiments and experimental data were described by Freundlich and Langmuir isotherm models. However, Langmuir adsorption isotherm model was able to best describe the adsorption of Cr(VI) ions on raw and modified forms of CNTs and AC.

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