

Comparison between activated carbon and multiwall carbon nanotubes in the removal of cadmium(II) and chromium(VI) from water solutions

Ali Naghizadeh

ABSTRACT

This paper evaluates the aqueous cadmium(II) and chromium(VI) adsorption efficiency on multiwall carbon nanotubes and activated carbon (AC). The effects of pH, initial metal ion concentrations, and adsorbent dosage on the adsorption of heavy metal by carbon adsorbents were also evaluated. In addition, this study used the Langmuir and Freundlich isotherms to describe behavior of equilibrium adsorption. It has been shown that the carbon nanotubes (CNTs) sampled exhibited a pH of point of zero charge (pH_{pzc}) of around 6.1 while the AC sample had a pH_{pzc} of about 6.8. Maximum adsorption efficiencies were found at pH 3 for both CNTs and AC. Also, carbon nanotubes have higher adsorption efficiency towards both studied metal ions in comparison with ACs. The capacity of CNTs to adsorb Cd(II) and Cr(VI) was 4.5 and 3.1 mg/g, respectively. Additionally, the capacity of AC to adsorb Cd(II) and Cr(VI) was 2.8 and 2.4 mg/g, respectively. The adsorption percentage of metal ions onto both carbon adsorbents increased as adsorbents dosage and initial metal ion concentrations increased. The equilibrium adsorption of the studied metal ions is best fitted using the Freundlich isotherm.

Key words | activated carbon, adsorption capacity, carbon nanotubes, metal ions

Ali Naghizadeh

Department of Environmental Health Engineering,
School of Public Health,
Birjand University of Medical Sciences (BUMS),
Birjand,
Iran
E-mail: al.naghizadeh@yahoo.com

INTRODUCTION

The presence of heavy metal ions in groundwater and seawater attract much attention due to their adverse effects on public health and ecological systems (Aklil *et al.* 2004; Wang *et al.* 2010).

The main sources of these metals are: mining; metallurgical manufacturing; tanneries; battery manufacturing industries; fossil fuels; the chemical industry and its reliance on catalysts, many of which are metals or metal compounds; and the production of plastics, such as polyvinyl chloride, which involve the use of metal compounds particularly as heat stabilizers, etc. The effects of heavy metals, such as copper, lead, zinc, mercury, chromium(VI) and cadmium, on human health have been investigated extensively (Nordberg *et al.* 2007; Gupta *et al.* 2011b; Saleh & Gupta 2012).

A need for efficient methods of removing metal ions from wastewaters before release into the environment is a matter of concern because of their toxicities in relatively

low concentrations and tendency toward bioaccumulation (Viard *et al.* 2004).

To remove toxic heavy metals from water systems, several methods have been investigated and suggested. Although chemical precipitation, coagulation, ion exchange, solvent extraction, filtration, evaporation and membrane methods have been applied to this purpose, most of these techniques have some limitations such as requirement of several pre-treatments or additional post-treatments (Kam *et al.* 2002). Adsorption is one of the extensively used methods for the removal of various compounds from aqueous solutions (Mittal *et al.* 2005; Gupta *et al.* 2006a, b).

Carbonaceous materials have been proved to be effective sorbents for the removal of metal ions as well as their complexes. Activated carbon (AC) is a common sorbent consisting of graphene sheets randomly substituted with hetero-atoms (Vidic *et al.* 1997). On the other hand, carbon

nanotubes (CNTs) have attracted much attention in the field of heavy metal ion removal because of their large specific surface area, small size, and hollow and layered structures (Chen & Wang 2006). Multiwall carbon nanotubes (MWCNTs) were previously used for the removal of metal ions, such as lead, copper, cadmium, silver, nickel (Li *et al.* 2003). Li *et al.* (2004) reported that CNTs had high adsorption efficiency for lead removal from water and the adsorption of lead was higher than copper and cadmium, and significantly influenced by the pH of the solution. Hsieh & Horng (2007) found that the adsorption capacity of CNTs grown on aluminum oxide, for the removal of Pb^{2+} , Cu^{2+} and Cd^{2+} from solutions is superior to those of active carbon powders, commercial CNTs, and aluminum oxide.

The aim of this work is to prepare a comparative study of carbon-based sorbents (AC, MWCNTs) in order to establish, for the first time, the existing similarities and differences between these materials concerning their application for removal and enrichment of selected metal ions. Cr(VI) and Cd(II) were taken as model metal ions.

EXPERIMENTAL

Materials

AC with an average diameter between 0.15 and 0.2 mm, and MWCNTs with an outer diameter of 20–50 nm and purity above 95% were obtained from the Research Institute of Petroleum Industry, Tehran, Iran. Prior to use, in order to purify AC and MWCNTs, the sorbents were dissolved in 37% hydrochloric acid solution for about 16 h at ambient temperature. The solution was filtered through a 0.45 μm membrane filter and the sorbents were washed several times with distilled water until the solution's pH was adjusted to approximately neutral. The treated sorbents were dried in a vacuum at 40 °C overnight. For eliminating the amorphous carbons, the purified sorbents were placed in a furnace at 400 °C for 30 min (Naghizadeh *et al.* 2013a).

High purity water was obtained from an ultra-pure water system. All glassware used in these experiments was acid-washed prior to use with nitric acid 5 wt.%, 24 h, and ultra-pure water was used to avoid the metal ions adsorbed on the flask wall.

The metal solutions were prepared from a 1,000 mg/L stock solution. The concentration of metals was determined by atomic absorption spectrometry using a PerkinElmer 3110 apparatus with the manufacturer's instrumental settings.

Characterization of the sorbents

To verify the desired structure of the synthesized sorbents, a scanning electron microscopy (SEM) image was taken with a Camscan MV2300 Microscope. Structural features were investigated by Raman spectroscopy (JobinYvon T-64 000), and X-ray diffraction (XRD) (Philips Analytical PC-APD) was used for characterization of the sample.

Point of zero charge

The pH of point of zero charge, pH_{PZC} , that is the pH above which the total surface of the carbon particles is negatively charged, was obtained by the following method: Two series of 50 mL deionized water in conical flasks were prepared with initial pH values in the range of 1–12. These pH values were adjusted by addition of concentrated hydrochloric acid for the acidic range and sodium hydroxide for the basic range, using a pH meter. About 20 mg of either AC or MWCNTs was placed in each conical flask of the series and left overnight to reach equilibrium at 25 °C. The final pH was then measured and plotted against the initial pH for each series. The pH at which the curve crosses the line, $\text{pH}(\text{final}) = \text{pH}(\text{initial})$, was taken as the pH_{PZC} of a given carbon sorbent.

Effect of pH

To study the effects of pH on the adsorption of metal ions including Cr(VI) and Cd(II) onto AC and MWCNTs, 50 mg of carbon material was dispersed into 100 mL solution containing 2 mg/L of each heavy metal ion. The initial pH values were adjusted from 3.0 to 11.0 using various amounts of HCl and NaOH and the suspensions were shaken for 4 h at 20 ± 1 °C. The amounts of adsorbed metal ions were calculated as the difference between the initial and final concentrations when the equilibrium was reached. The results are based on at least three replicate experiments for each pH value.

Kinetic studies

The kinetic investigations were carried out to study the time required for the attainment of equilibrium during the adsorption of Cr(VI) and Cd(II) on AC and MWCNTs in aqueous solutions.

In all of the adsorption tests, 50 mg of AC or MWCNTs as adsorbents were placed in the bottles and 100 ml of solution containing a specific amount of metal ions were added to the adsorbents (concentration range 0.5–2 mg/L). After shaking for 4 h at 20 ± 1 °C, the metal concentration in the aqueous solutions was determined by atomic absorption spectrophotometer. The sorption capacity q (mg/g) was obtained as follows:

$$q = [(C_0 - C_f)V/M] \quad (1)$$

where C_0 and C_f are the initial and final concentrations (mg/L) of metal ions in the aqueous solution, respectively, V is the volume of metal ion solution, and M is the weight of adsorbent.

Adsorption equilibrium isotherms

In this work, attempts have been made to analyze adsorption using Freundlich and Langmuir models. The linear regression was used to determine the best fit model between the two studied isotherms. Equations (2) and (3) express the

Freundlich and Langmuir isotherms, respectively

$$Q_e = \frac{Q_{\max}K_L C_e}{1 + K_L C_e} \quad (2)$$

$$Q_e = K_F C_e^{1/n} \quad (3)$$

where Q_e (mg/g) is the equilibrium metal ion concentration in the solid phase; Q_{\max} (mg/g) is the maximum amount of sorption; K_L (L/mg) is the Langmuir sorption equilibrium constant; C_e is the concentration of solute at equilibrium or after adsorption; K_F ($\text{mg}^{1-1/n}\text{L}^{1/n}/\text{g}$) is the Freundlich constant representing the sorption capacity, and n is the constant depicting the sorption intensity. K_F and n must be evaluated for each solute and temperature, and are related to adsorption capacity and energy of adsorption.

RESULTS AND DISCUSSION

Characteristics of AC and MWCNTs

For accurate determination of the diameter of AC and MWCNTs bundles, SEM was used. This technique gives information mainly regarding the surface morphology of AC and nanotube samples. SEM images (Figure 1) show that carbon materials have very distinct morphological features. It can be ascertained from the figure that MWCNTs

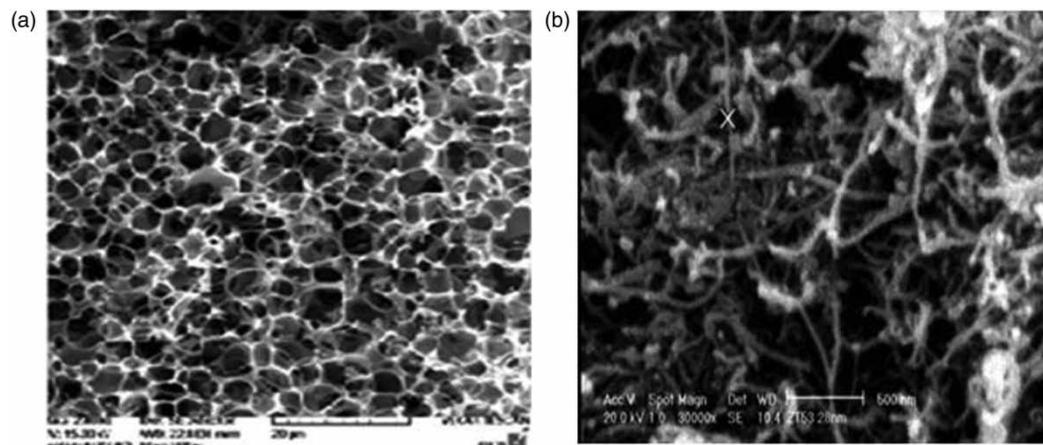


Figure 1 | SEM images of (a) AC and (b) CNTs.

have diameters in the range 20–50 nm and lengths of up to several microns. AC appears as relatively large grains (150–200 μm) with well-defined sharp edges. The edge planes have a very regular porous structure with a narrow diameter distribution.

The Raman spectra of AC and MWCNTs are shown in Figure 2. As can be seen in the figure, the spectra were collected in the range 1,000–2,400 cm^{-1} . Two bands appear in the spectra. The first band on the left of the figure, called D band, originates from a hybridized vibrational mode associated with graphene edges and disorder, and becomes active when the crystallinity decreases (Equation (2)), for example, in the presence of defects and finite size effects. The G band corresponds to the stretching vibrations with the basal graphene layers in all carbon materials. Its width is also related to the stacking ordering between the adjacent graphene layers (Yoshida *et al.* 2006).

Raman spectroscopy can evaluate amorphous components or the amount of defects based on the ratio of the G-band to the D-band (G/D ratio). This ratio is a useful indicator of the sample crystallinity (Wang *et al.* 1990).

The values of G/D ratios are given in Table 1. According to Figure 2, MWCNTs have higher crystallinity and ordering between the graphene layers than AC. AC is a material with a very short range of crystallinity. The observed G/D ratio for AC is typically related to amorphous carbon materials (Bystrzejewski *et al.* 2008).

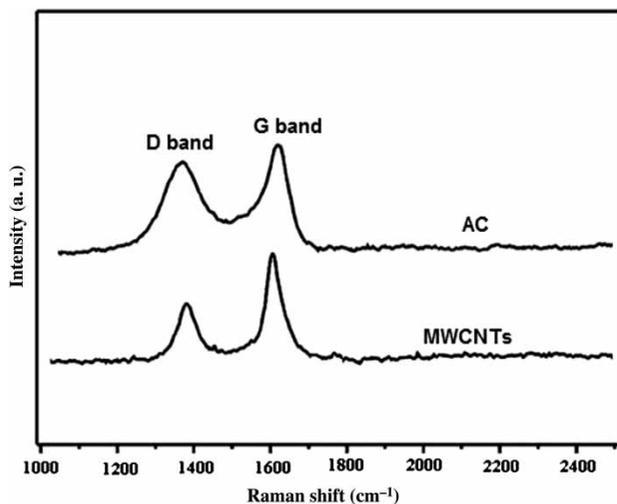


Figure 2 | Raman spectra of AC and MWCNTs.

Table 1 | Surface properties of MWCNTs and AC

Adsorbents	G/D ratio	S _{BET}	pH _{pzc}
MWCNTs	1.53	130.52	6.1
AC	0.56	143.71	6.7

Figure 3 shows the XRD spectra for both AC and MWCNTs. The peaks at 26° and 44° for MWCNTs, and 28° and 48° for AC relate to graphene structures of carbon adsorbents. These findings agree with earlier findings (Naghizadeh *et al.* 2013b).

Determination of pH_{pzc} and effect of pH

As shown in Figure 4, the MWCNTs sample exhibited a pH_{pzc} of around 6.1 while the AC sample had a pH_{pzc} of around 6.7. These results indicate that MWCNTs samples are negatively charged when exposed to pH > 6.1, while the AC samples become negative for pH > 6.7. These

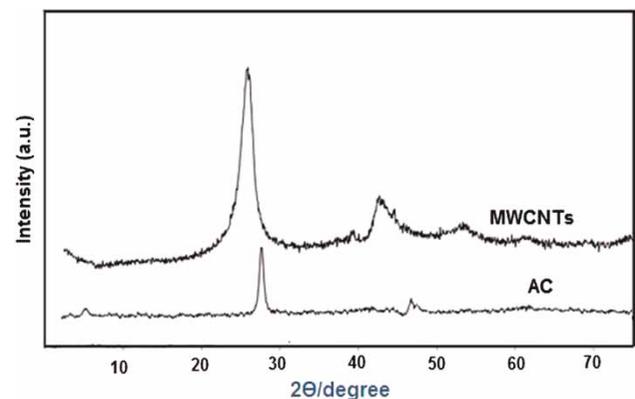


Figure 3 | XRD spectra of AC and MWCNTs.

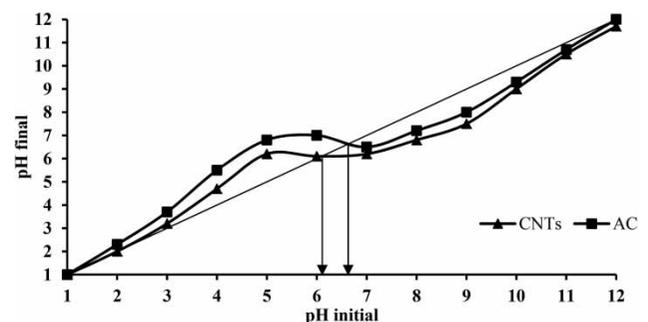


Figure 4 | Determination of pH_{pzc} for MWCNTs and AC.

results are in agreement with those Naghizadeh *et al.* (2013b) had previously observed on MWCNTs samples. They found that the point of zero charge, pH_{pzc} , of raw MWCNTs was 6.1.

Figure 5 shows the effect of pH on adsorption of Cr(VI) and Cd(II) on AC and MWCNTs. The pH was varied from 3 to 12 while keeping the initial concentrations relatively constant (2 mg/L).

Figure 5 shows that the uptake of chromium(VI) by MWCNTs and AC was highly pH dependent. Maximum adsorption efficiencies of 3.1 and 2.5 mg/g were found at pH 3 for MWCNTs and AC, respectively. The variation in removal efficiency at different pH values may be attributed to the affinities of MWCNTs and AC for different species of Cr(VI) existing at acidic pH values, namely $H_2CrO_4^0$, CrO_4^{2-} , CrO_4^{2-} , and $Cr_2O_7^{2-}$ (Gupta *et al.* 2011a). Cr(VI) uptake decreased slightly with increasing pH because of the higher concentration of OH^- ions present in the reaction mixtures. Similar findings have been reported in the literature for the sorption of chromium onto magnetite-maghemite nanoparticles (Chowdhury & Yanful 2010).

As can be seen in Figure 5, the adsorption capacity of Cd(II) presents an increasing trend with the rise in pH value. The higher adsorption efficiency at higher pH may be due to the precipitation of metal hydroxides on the adsorption sites. This would decrease the equilibrium concentration of metal ions and suggest higher metal uptakes (Heine & Van Der Linden 1978). These findings are in accordance with previous studies which reported higher adsorption capacities for Cd(II) in higher pH solution (Wu 2007; Kuo & Lin 2009).

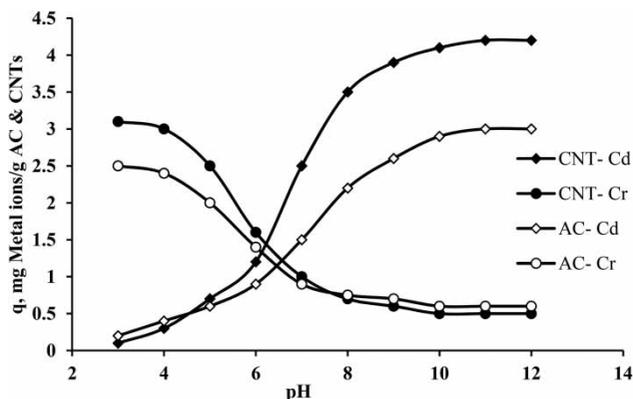


Figure 5 | Effect of pH on adsorption of metal ions onto carbon adsorbents.

Effect of contact time and initial concentration

Figure 6 shows the effect of contact time on removal of chromium and cadmium by MWCNTs and AC. Experimental studies were carried out with varying initial metal ion concentrations of chromium and cadmium in the range 0.5–2 mg/L using 20 mg of adsorbent dose at optimum pH.

The amount of metal ions adsorbed onto carbon adsorbents increased with contact time for all metal ion concentrations. The curves reveal that the adsorption kinetics of metal ions on carbon adsorbents mainly consists of two stages: an initial rapid stage related to the instantaneous external surface adsorption of metal ions. The second slower stage is the gradual adsorption stage that takes place before metal ion uptake attains equilibrium. The high adsorption rate during the initial period of 20 min is due to the number of available adsorption sites of the bare surface of the adsorbents. As the sites became progressively covered, the rate of adsorption decreased. According to these results, the agitation time was fixed at 45 minute for the rest of the batch experiments to make sure that equilibrium was attained. Similar findings have been reported in the literature (Rao *et al.* 2006).

The results show that the agitation time required for maximum uptake of metal ions by carbon adsorbents was dependent on the initial metal ions concentrations. The equilibrium time is important because of its direct relationship to economical application in wastewater treatment plants (Kadirvelu & Namasivayam 2003).

The fraction of metal ions that were adsorbed onto MWCNTs at an initial concentration of 2 mg/L, reached 4.5 and 3.1 mg/g for Cd(II) and Cr(VI), respectively. The fraction of metal ions that were adsorbed onto AC reached 2.7 and 2.3 mg/g for Cd(II) and Cr(VI), respectively. This can be attributed to the higher adsorption capacity of CNTs due to higher volumes of mesopores in comparison with AC.

Adsorption isotherms

Figure 7 represents the adsorption isotherms of Cd(II) and Cr(VI) at optimum pH as a relationship between the amount of metal ions adsorbed per unit mass of AC and MWCNTs and the equilibrium concentration of the metal ion in aqueous solution. The adsorption capacity determines

how much adsorbent is required for quantitative enrichment of the analyte from a given solution. The fitted parameters using Freundlich and Langmuir models are listed in Table 2. The theoretical isotherm curves are compared with the corresponding experimental observations for cadmium and chromium adsorption onto MWCNTs and AC, respectively. According to Figure 7 and Table 2, the Langmuir isotherm was not found to be suitable as evidenced from the value of the regression coefficients (R^2). The Freundlich empirical model describes well adsorption on heterogeneous surfaces and is often used for cases of heavy metal sorption onto carbon materials (Boehm 2002; Li *et al.* 2003; Stafiej & Pyrzyńska 2007; Yuzer *et al.* 2008).

Generally in the Freundlich model, K_F increases as the adsorption capacity of the adsorbent increases and $1/n$ decreases as the adsorption strength increases.

Cadmium ions are more favorably retained onto MWCNTs and its adsorption capacity attained 4.1 mg/g at an initial concentration of 4.0 mg/L, while the highest adsorption capacity for Cr(VI) onto MWCNTs was obtained at about 3.2 mg/g. Metal ions (both Cd(II) and Cr(VI)) have a lower affinity towards the AC compared with nanotubes; the adsorption capacities for Cd(II) and Cr(VI) onto AC were 2.9 and 2.4 mg/g, respectively. Generally, the isotherms were fitted very well by linear regression analysis as this is confirmed by the comparison of R^2 values, which

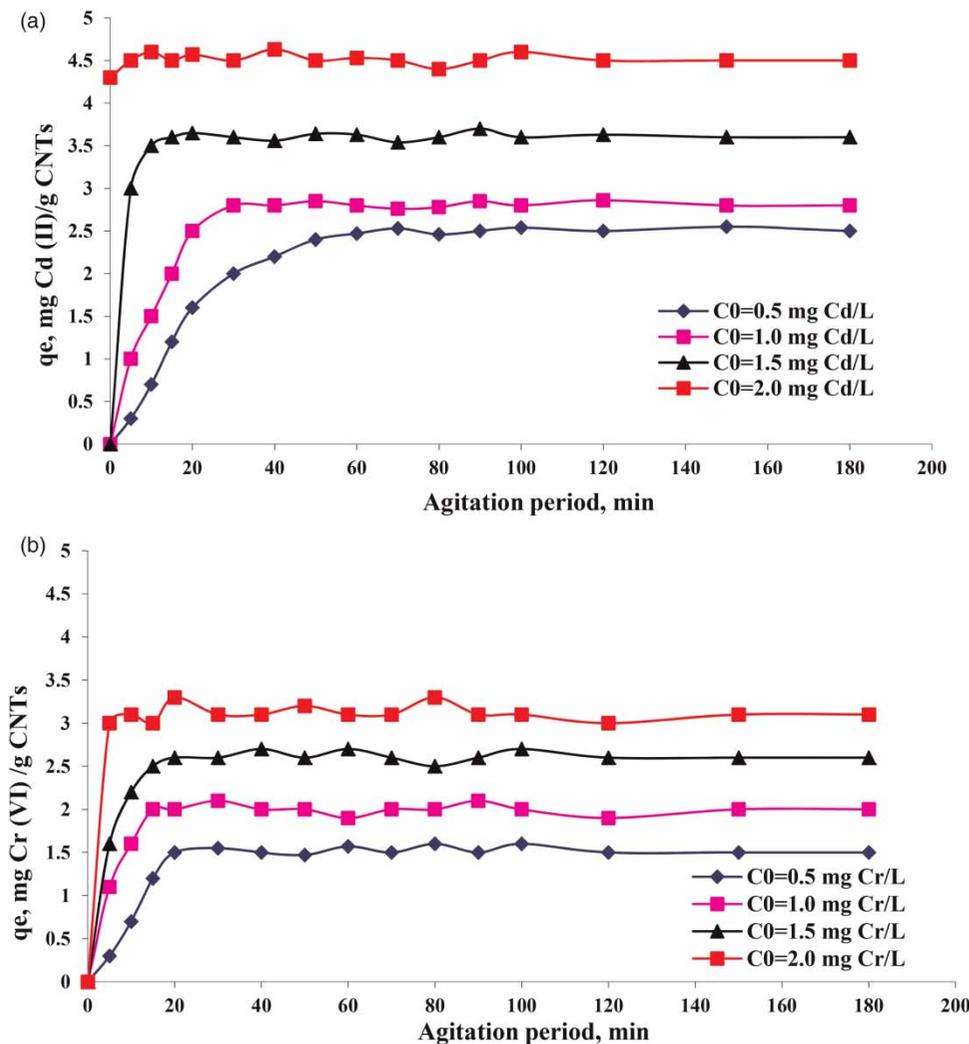


Figure 6 | Effect of initial concentration and contact times of metal ion adsorption onto AC and CNTs at optimum pH (optimum pH for Cr(VI) = 4 and for Cd(II) = 10). (continued)

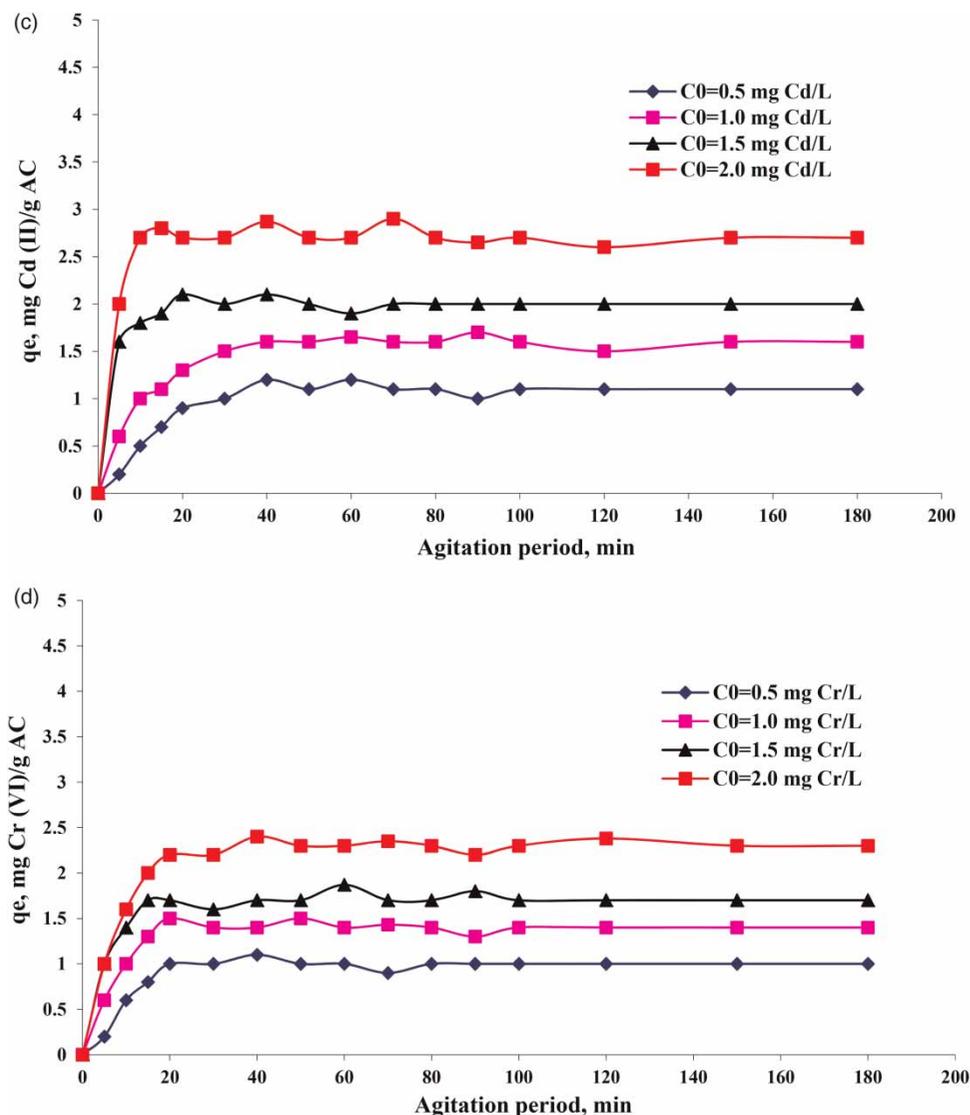


Figure 6 | continued

all are >0.98 . The highest sorption capacity for both studied ions is found for CNTs in comparison with AC. These findings are in accordance with the previous literature data (Naghizadeh *et al.* 2011; Dehghani *et al.* 2013).

There are many studies that provide adsorption capacities of different metal ions both for CNTs and AC. But the comparison of the previous literature data with our results may lead to substantial uncertainties. These ambiguities are because previous literature results are achieved from adsorbents with a different structure (e.g. surface acidity, surface area) and distinct experimental conditions (e.g. pH). As an

example, the adsorption capacities of Cd(II) onto CNTs can be between 2.4 and 42 mg/g (Kuo & Lin 2009; Chowdhury & Yanful 2010). A comparable discrepancy is also considered for the same metal ion and AC. The adsorption capacities are in the range between 0.1 and 24 mg/g (Dianati-Tilaki & Ali 2003; Rao *et al.* 2006; Hema & Srinivasan 2011).

Effect of carbon adsorbents dosage

The masses of carbon adsorbents used in the removal of metal ions from aqueous solution are critical for the

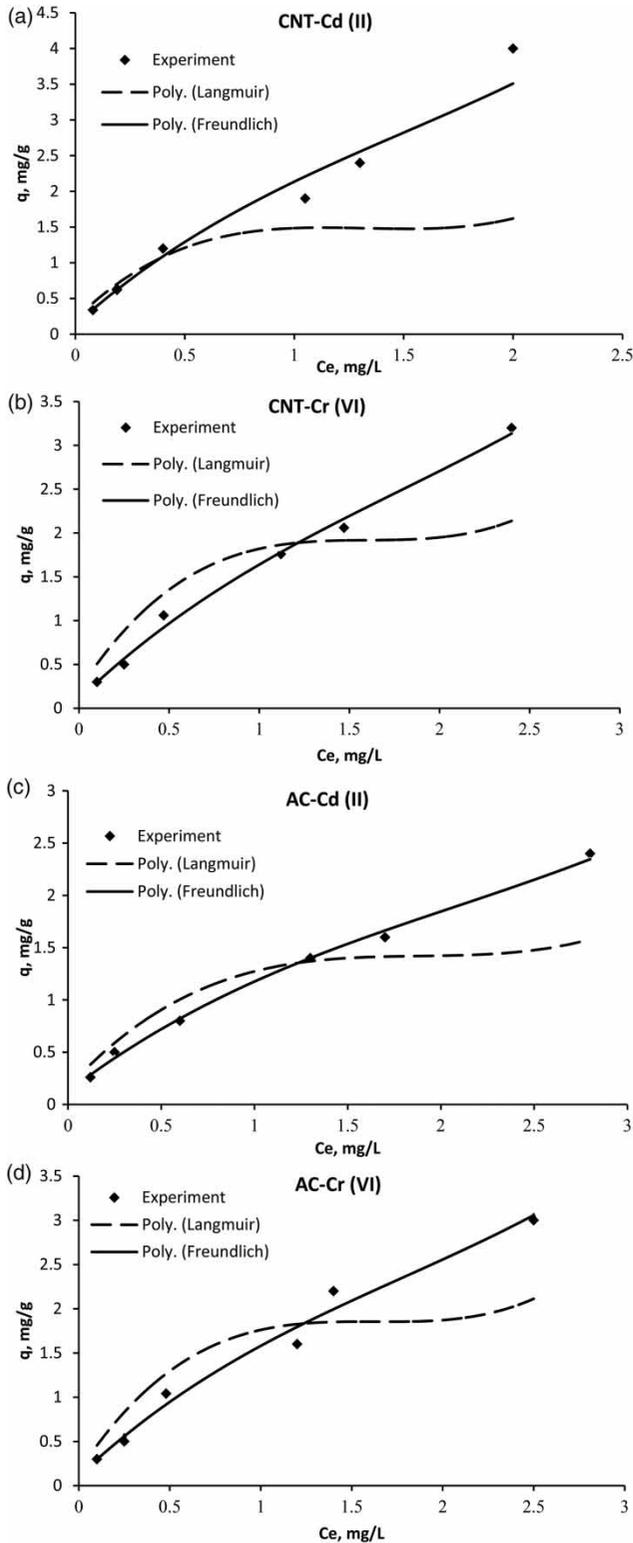


Figure 7 | Adsorption isotherms of metal ions onto AC and CNTs.

Table 2 | Parameters of Freundlich and Langmuir isotherm models for sorption of metal ions

Adsorbents-Metals	Freundlich			Langmuir		
	K_f (mg/g) (mg/L) ⁿ	n	R^2	q_m (mg/g)	b (L/mg)	R^2
CNTs						
Cd(II)	2.11	1.37	0.99	1.84	3.5	0.70
Cr(VI)	1.62	1.33	0.99	2.3	2.5	0.84
AC						
Cd(II)	1.16	1.46	0.99	1.86	1.97	0.90
Cr(VI)	1.56	1.36	0.98	2.08	2.51	0.83

application of these adsorbents in metal ion elimination. If amounts of adsorbents used in the removal of metal ions are high, then the cost of using these adsorbents would be high and they cannot be used extensively. The effect of adsorbent dosage on removal of chromium and cadmium has been presented in Figure 8.

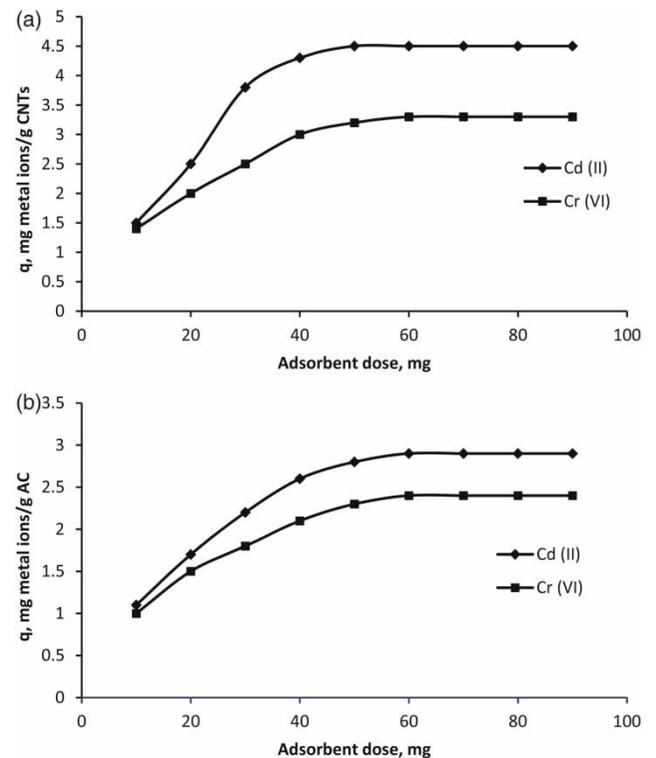


Figure 8 | Effect of adsorbent dose on removal of metal ions (initial concentration 10 mg/L).

The amounts of MWCNTs required for the complete removal of Cr(VI) and Cd(II) from 50 ml (10 mg/L) of aqueous solution were 0.11 and 0.16 g, respectively. The amounts of AC required for removal of the above metal ions from the mentioned solution were 0.17 and 0.20 g, respectively. This increase in percent removal of heavy metal ions with increasing in the concentration of the AC and MWCNTs is due to the greater availability of the exchangeable sites or surface area at higher concentrations of the adsorbent (Rengaraj & Moon 2002; Ren *et al.* 2011).

CONCLUSION

In this study, adsorption of Cd(II) and Cr(VI) ions onto MWCNTs and AC was studied. The effects of adsorption parameters, such as adsorbent dosage, pH, metal ion concentration, and adsorption isotherm were studied and optimized. Adsorption efficiency was investigated for metal ions in a broad pH range (3–12). Both carbon adsorbents showed higher adsorption capacities for Cd(II) and Cr(VI) in basic and acidic conditions, respectively. The equilibrium adsorption of metal ions on AC and MWCNTs was studied and the adsorption isotherms were well described by Freundlich isotherm models. The results revealed that MWCNTs had a greater potential for the removal of target metal ions from aqueous solution samples than AC.

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