

Multi-walled carbon nanotubes as adsorbents for the removal of parts per billion levels of hexavalent chromium from aqueous solution

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ABSTRACT

The adsorption capabilities for the removal of parts per billion levels (ppb) of hexavalent chromium by three adsorbents namely activated carbon, functionalised multi-walled carbon nanotubes (MWCNTs) and unfunctionalised multi-walled carbon nanotubes were investigated as a function of contact time, initial solution pH, initial Cr(VI) concentrations and the presence of competing anions. The unfunctionalised MWCNTs showed the highest adsorption capability with up to 98% of a 100 ppb Cr(VI) solution being adsorbed. Both functionalised and non-functionalised MWCNTs showed a superior adsorption capability to that of activated carbon. The removal of Cr(VI) was higher at lower pH. Furthermore, the uptake of Cr(VI) was hindered by the presence of the competing anions, Cl^- and SO_4^{2-} . Both Langmuir and Freundlich isotherms have been used to describe the Cr(VI) adsorption process. The major mechanisms for Cr(VI) removal have been identified as an ion exchange mechanism, intraparticle diffusion and electrostatic interactions. The adsorbed Cr(VI) could also be desorbed readily from the MWCNTs surface at high pH.

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1. Introduction

Hexavalent chromium (Cr(VI)) is extensively used in the leather tanning, electroplating, metal finishing and stainless steel industries [1–3]. Further, Cr(VI) is also well known for its toxic effects in a multitude of cancers, mucosal ulcerations, kidney disorders and chronic dermatitis [4–7]. Such toxicity has warranted the need for the efficient and complete removal of Cr(VI) from industrial wastes.

Several treatment technologies have been implemented for the removal of Cr(VI). These include precipitation, membrane filtration, ion exchange and adsorption by activated carbon and various other adsorbents including biological adsorbents [8–15]. However, besides adsorption by activated carbon, these methods have proven to be expensive, time consuming, rather inefficient, not very feasible for small scale industries and have resulted in the production of undesirable sludges [8,10–18,25]. Cr(VI) can also have toxic and inhibitory effects on the biological organisms that are used as biosorbents [19,20]. Sometimes regeneration

efficiencies of the biosorbents and other adsorbents are not very good [21]. These methods have also not been very efficient for the removal of low concentrations of heavy metals [22].

Cheaper alternatives to activated carbon such as wool, pine needles, olive cake, sawdust, almond shells, cactus leaves, palygorskite clay, cornelian cherry, apricot stones and charcoal have been explored but these have not been as efficient as activated carbon [11,23,24]. Furthermore, whilst certain forms of activated carbon containing ppb (parts per billion) and ppm (parts per million) levels of impurities have shown a potential to remove trace concentrations of Cr(VI) [62], activated carbon has generally not been able to reduce the concentrations of contaminants at ppb levels [25]. It is known to only adsorb a few milligrams of adsorbent per g of activated carbon, adsorb moisture, present problems with the adsorption of hydrophilic substances, to lose its adsorption efficiency and also poses problems with regeneration [25,26]. High quality activated carbon is expensive [18,25]. Activated carbon is known to be unselective for the adsorption of inorganic contaminants due to its non-polar surface [25]. The adsorption equilibria are also attained very slowly in activated carbon due to slow pore diffusion [27,28].

Carbon nanotubes are a relatively new form of carbon which was brought to prominence by studies in the early 1990s [29].

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A carbon nanotube is essentially a sheet of graphite that has been rolled into a tubular form. Two types of carbon nanotubes may be distinguished depending on the number of outer layers on the tubular structure. These are single walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs).

SWCNTs are expensive and difficult to purify [30]. In contrast, MWCNTs are readily synthesised in good purity and yield, and are much cheaper than SWCNTs.

In 2004 the US Environmental Protection Agency (EPA) expressed a need for the environmental applications of carbon nanotubes to be explored [29] and remediation or treatment was identified as one of the key areas that needed to be investigated. Since then carbon nanotubes have been gaining increasing recognition for their adsorption capabilities. This is due mainly to their extremely small size, uniform pore distribution and large specific surface area [25,29]. It has also been stated that their well-defined porosity and functionality renders them superior adsorbents to other adsorbents like activated carbon [29]. The nanotube surfaces may also be chemically modified to enhance the adsorption of specific ions or molecules. In other words certain functionalities or defect sites on the nanotube surface may play a role in the adsorption of molecules and ions [29].

The US EPA has expressed an interest in monitoring trace levels of chromium and arsenic in the environment [29] as hexavalent chromium becomes lethal when it reaches a concentration of 0.1 mg g^{-1} body weight [31]. The National Institute for Occupational Safety and Health (NIOSH) has even recommended that the amount of chromium in water should be limited to $10^{-3} \text{ mg m}^{-2}$ [32]. The maximum allowable concentration in drinking water has been set at 50 ppb [33,34].

The environmental applications of carbon nanotubes that have been investigated thus far include studies on the storage of gases like hydrogen as well as the removal of metal ions and organic contaminants [29,35]. Both functionalised and unfunctionalised single walled carbon nanotubes (SWCNTs) have shown a superior adsorption capacity to that of activated carbon for the uptake of Pb(II), fluorides and dioxins [35–37]. Recently multi-walled carbon nanotubes (MWCNTs) have also been used as adsorbents for chlorophenols, removal from environmental water samples [38] and even for the removal of Pb^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} [27,39]. Di et al. [40] have also shown that ceria nanoparticles supported on aligned carbon nanotubes are effective in the removal of Cr(VI). Qui and Li [41] have shown that multi-walled carbon nanotubes were six times more efficient at removing a 190 ppm Cr(VI) solution than activated carbon.

However, apart from the study undertaken by Dobrowolski and Stefaniak [62] most studies that have reported the uptake of metal ions including Cr(VI) by carbon nanotubes and other adsorbents have focussed on the uptake of such ions in the parts per million concentration range (usually above 100 mg L^{-1}) [25] and not for trace concentrations, i.e. the parts per billion concentration range. The lowest concentrations used thus far are in the 0.05–10 ppm range [16,42–46]. Some authors have hinted at the possibility of applying biosorption systems for the removal of lower concentrations of Cr(VI) but have not explored this any further [47]. Some relevant studies on biosorption pertinent to this work have been reported [22,34,45,48,49].

The purpose of this study was to establish whether multi-walled carbon nanotubes (both functionalised and unfunctionalised) can act as efficient adsorbents for ppb concentrations of Cr(VI) from aqueous solution. A comparative study using activated carbon as an adsorbent was also undertaken. The effect of contact time, initial solution pH, initial Cr(VI) concentration and competing anions was investigated.

2. Materials and methods

2.1. Adsorbents

2.1.1. Functionalised MWCNTs

The functionalised MWCNTs were purchased from SUNNANO™. These MWCNTs had a purity of >90% and a diameter of 10–30 nm. An IR spectrum of these nanotubes was run to verify the presence of the electron rich functional groups such as hydroxyl and carboxyl groups (see Fig. A1).

2.1.2. Unfunctionalised MWCNTs

Unfunctionalised MWCNTs were synthesised at the University of the Witwatersrand by the chemical vapour deposition method over a Fe/CaCO₃ catalyst [50].

2.1.3. Activated carbon

The powdered activated carbon was commercially obtained from Merck. This was already purchased in the activated form but was further activated with KOH. This type of activation is usually conducted at 800–1000 °C in order to develop a basic surface oxide layer and to raise the solution pH [25]. This method of activation also increases the activated carbon surface area and pore volume.

2.1.4. Chemicals

A 1000 ppm stock Cr(VI) solution was prepared by dissolving 2.874 g K₂Cr₂O₇ (analytical grade) in 1 L distilled water. This solution was diluted to 1000 ppb which was in turn diluted to a 100 ppb Cr(VI) solution. Solutions of 0.1 M HCl and 0.1 M NaOH were used for pH adjustment.

2.2. Batch adsorption experiments

For the batch adsorption experiments, 0.1 g of each adsorbent was weighed out and placed in contact with 10 mL of the 100 ppb Cr(VI) solution in sample vials. The adsorbents were placed in contact with the Cr(VI) solution for contact times of 1, 2, 3, 4, 6, 8, 12 and 24 h, respectively.

Contact between the adsorbents and the Cr(VI) solution was facilitated by agitation on a shaker. After each specified contact time, the Cr(VI)-adsorbent suspension was filtered through a 0.45 μm EconoClear filter, commercially obtained from Microsep. The filtrates were retained for analysis of their Cr(VI) content by Adsorptive Stripping Voltammetry.

To investigate the influence of pH, the adsorbents were placed in contact with the Cr(VI) solution and the pH was adjusted using either 0.1 M HNO₃ or 0.1 M NaOH. All samples were agitated on a shaker for a contact time of 12 h. The pH was varied across the entire pH scale.

The influence of the initial Cr(VI) concentrations was investigated by preparing standard solutions of Cr(VI) ranging from 100 to 3000 ppb. These solutions were left in contact with 0.1 g of the adsorbent for 12 h with agitation on a shaker.

The effect of competing anions was examined by spiking the Cr(VI)-adsorbent suspensions with 0.1 M sodium sulphate where the sulphate ions which are chemically similar to the dichromate ions would act as competing anions. In a separate experiment, the Cr(VI)-adsorbent suspensions were also spiked with a 0.1 M sodium chloride solution where the chloride ions could also act as potential competing ions. These suspensions were agitated on a shaker for contact times of 1, 2, 3, 4, 6, 8, 12 and 24 h, respectively.

2.3. Desorption experiments

Desorption and regeneration was explored on these materials. To investigate the possibility of regeneration, desorption experi-

ments were conducted where 0.1 g of each type of MWCNT was kept in contact with 10 mL of 100 ppb $K_2Cr_2O_7$ solution for 24 h in order to ensure that maximum adsorption was achieved. The pH in this case was maintained at 7. After this equilibration time, the suspension was centrifuged and filtered. The remaining MWCNT residue onto which Cr(VI) had been adsorbed was subsequently washed with 100 mL distilled water once after 1, 2, 3, 4, 6, 8, 10, 12 and 24 h, respectively. These desorption experiments were repeated using 0.1 M NaOH as a washing agent. Samples were collected after each wash and analysed on the MetroOhm Polarograph in order to determine how much Cr(VI) had desorbed.

2.4. Analysis

All filtrates collected from the adsorption and desorption experiments were analysed for their Cr(VI) content using a MetroOhm polarograph in the Adsorptive Stripping Voltammetry mode. This method was selected since it is not only speciation specific to Cr(VI) but is also highly sensitive to parts per billion levels of Cr(VI) where the lower limit of detection is said to be $0.5 \mu\text{g L}^{-1}$ [42]. The background electrolyte used for this study was prepared by dissolving 21.2 g NaNO_3 , 1.968 g diethylenetriamine pentaacetate (DTPA) and 0.16 g CH_3COONa in distilled water in a 100 mL volumetric flask. The voltammetric parameters were set as follows:

Purge time: 300 s, conditioning time: 600 s, conditioning potential: 0 V, deposition potential: -1.0 V, deposition time: 60 s, equilibration time: 10 s initial potential: -1.0 V, final potential: -1.5 V.

Each sample was analysed by adding 2.5 mL of the sample, 1.5 mL of background electrolyte and 1 mL of deionised water to the voltammetric cell. NaOH (40%) was also added to adjust the pH to ± 6.2 . The pH was monitored using a MetroOhm pH meter. The samples were also analysed by the standard addition method where each sample was spiked with 1 μL increments of 1 ppm Cr(VI). Standard coefficients of 0.99 indicated good precision of the analytical results.

2.5. Quality assurance

A number of quality control steps were taken to ensure the reliability of the analytical data. Thus, all batch experiments were conducted in duplicate to check the reproducibility of the analytical data and average results are reported here. The analytical data was found to be reproducible with a relative error of $\pm 2\%$.

To verify that the decrease in Cr(VI) concentration was indeed due to adsorption by the various adsorbents, a blank experiment without the MWCNTs was run. The results of this experiment indicated that there was no change in Cr(VI) concentration with time.

The relative standard deviation of the analytical data was also determined to evaluate the accuracy of the data. This was found to be 5% thereby indicating good accuracy of the data.

2.6. Zeta potential measurements

Zeta potential measurements on each type of adsorbent were conducted on a Malvern Zetasizer. Basically the zeta potential was measured as a function of pH so that the point of zero charge (pH_{PZC}) of each adsorbent could be determined.

2.7. Brunauer-Emmett-Teller method (BET)

About 0.2 g of both the functionalised and unfunctionalised MWCNTs were degassed in nitrogen at 120°C for 4 h before undergoing analysis on a Micromeritics Flow Prep 060 sample degassing

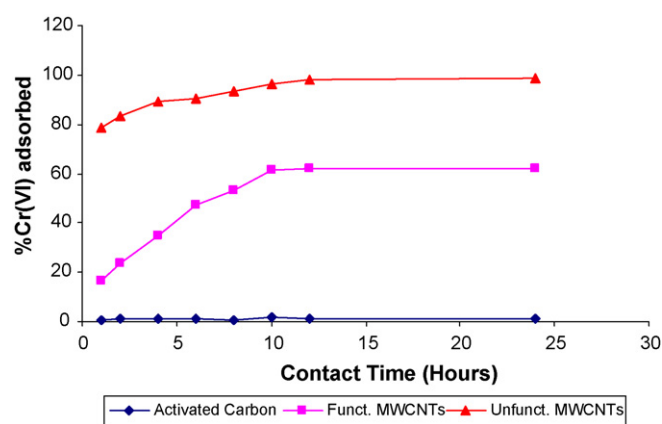


Fig. 1. The effect of contact time on the amount of Cr(VI) adsorbed by each adsorbent.

system. The surface areas and pore size distributions were measured at 120°C . The pore size distributions with specific surface areas of both types of MWCNTs were measured by N_2 adsorption/desorption according to the BET method on a Micromeritics Tristar, surface area and porosity analyser.

3. Results and discussion

3.1. Contact time

Fig. 1 shows the influence of contact time on the adsorption capacity of the MWCNTs (both functionalised and unfunctionalised) and activated carbon. Less than 1% adsorption by activated carbon was observed. According to the literature reports activated carbon is expected to have a poor adsorption capacity for ppb levels of contaminants [26,51]. This loss in adsorption effectiveness is thought to be due to the filling of pores by water [26]. Basically, Cr(VI) is a highly mobile form of chromium which can easily migrate into the moisture that is trapped in the pores and is therefore not very easily retained on the solid activated carbon surface. This argument is supported by the review article by Mohan and Pittman [26] where it is clearly stated that one of the disadvantages of using activated carbon is that it presents problems with the adsorption of hydrophilic substances.

Both types of MWCNTs, by contrast, show a good ability to remove Cr(VI) from aqueous solution and attain equilibrium within 12 h of contact time. The unfunctionalised MWCNTs however, show a greater ability (98% adsorption) to adsorb Cr(VI). Repeat experiments confirmed these results. From the IR spectrum of the functionalised MWCNTs (see Fig. A1) it is noted that there are hydroxyl groups (3436 cm^{-1} ; O–H stretching mode) present. To verify that the functional groups were indeed affecting the adsorption of Cr(VI), the functional groups were removed by heating the MWCNTs under argon in a tube furnace at 900°C for 9 h. An IR spectrum (not shown) verified that all the functional groups were indeed removed. Fig. 2 shows that the adsorption capability (96% adsorption in 12 h) of these MWCNTs improved significantly after the functional groups were removed and are similar to the adsorption capacity of the original unfunctionalised MWCNTs. This observation is in agreement with the literature reports for the uptake of Cr(VI) by activated carbon which have been functionalised or oxidised [52]. Park and Jang [53] also showed that the adsorption of Cr(VI) onto a carbon surface decreased in the presence of oxygen surface complexes. There is a possibility that some reoxidation of the MWCNTs could have resulted after the heating process. However, the IR data showed no evidence for the presence of acid.

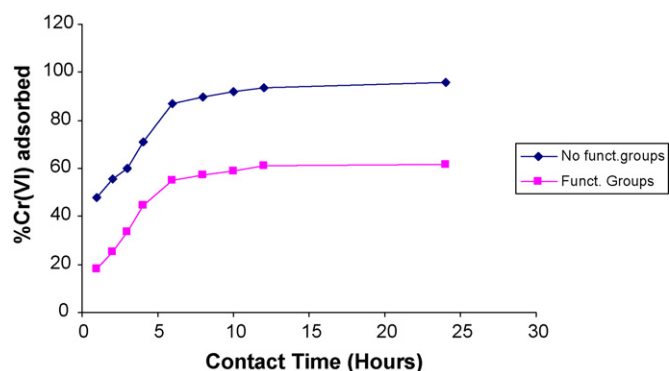


Fig. 2. The adsorption capability of the functionalised MWCNTs after the functional groups had been removed.

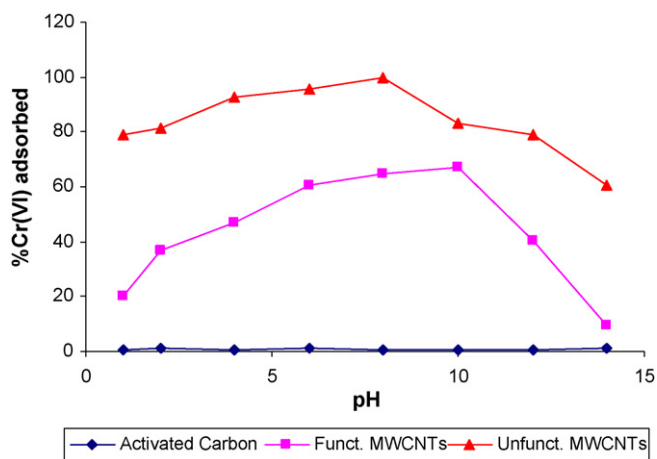


Fig. 3. The effect of pH on the uptake of Cr(VI) by the three adsorbents.

3.2. Initial solution pH

Fig. 3 shows the influence of initial solution pH on the adsorption capacity of all three adsorbents. It must be borne in mind that at low pH (<3) Cr(III) is the thermodynamically stable form of chromium, not Cr(VI) [15,40,58–60]. This is verified by the Eh–pH diagram of Cr(VI) which shows that the predominant form of Cr(VI) at low pH is indeed Cr^{3+} . Beukes et al. [61] also showed that the reduction of Cr(VI) to Cr(III) was very rapid at low pH and reported a pK_a value of 2.4. Thus, at lower pH it is actually Cr(III) in the form of polymerised Cr oxides [15,53] that is being adsorbed. A possible explanation for

the adsorption that is taking place could be competition between Cr(III) ions and H^+ ions for active sites on the MWCNT surface. Other workers have reported similar phenomena for the uptake of Cr(VI) by activated charcoal [58]. The results therefore suggest that all the chromium regardless of whether it is present as Cr(III) or Cr(VI) can be removed. The Eh–pH diagram also shows that some Cr(VI) can also exist as HCrO_4^- at low pH. Thus some of these species are also adsorbed at low pH. So, in a typical industrial waste the MWCNTs can remove both forms of chromium by the adsorption process.

Activated carbon still shows no significant affinity for Cr(VI). Both types of MWCNTs show a high adsorption capacity at low initial pH, and a diminishing adsorption capacity at higher initial pH with the maximum adsorption being attained at ca. pH 6. Clearly, this can be explained in terms of surface charge; a positive surface charge facilitates the adsorption of dichromate ions as suggested in the literature [15,44,54–57].

The redox mechanisms must also be carefully considered. Cr(III) forms at lower pH as a result of the reduction of Cr(VI) to Cr(III). Such a reduction is coupled to the oxidation of carbon surfaces resulting in carboxyl surface moieties [59]. Thus, it can be argued that there are carboxyl functionalities on the oxidised carbon nanotube surface which are binding and adsorbing Cr(III) at low pH.

3.2.1. Point of zero charge (pH_{PZC})

As indicated in Section 2.6 the zeta potentials of each type of adsorbent was measured as a function of pH in order to determine the point of zero charge (pH_{PZC}) of each adsorbent. Fig. 4 shows the zeta potential curves for each type of adsorbent. From these curves it can be seen that the pH_{PZC} is around 3.8, 7 and 8.5 for activated carbon, the unfunctionalised and functionalised MWCNTs, respectively. The fact that activated carbon has the lowest pH_{PZC} suggests that its surface charge is the most negative. This further explains why its adsorption capacity is so poor. The negative surface charge facilitates electrostatic repulsion of the dichromate ions. On the other hand, the unfunctionalised MWCNTs have the highest pH_{PZC} implying that it has a more positive surface charge compared to the other two adsorbents. This favours the adsorption of the negatively charged dichromate ions. The difference in pH_{PZC} between the functionalised and unfunctionalised MWCNTs also accounts for the difference in their adsorption capacities. The pH_{PZC} of the functionalised MWCNTs is lower which implies that it has a more negative surface charge which hinders the adsorption of the negatively charged dichromate ions.

3.3. BET surface area and porosity measurements

As indicated in Section 2.7 surface area and pore size measurements were recorded on the functionalised and unfunctionalised

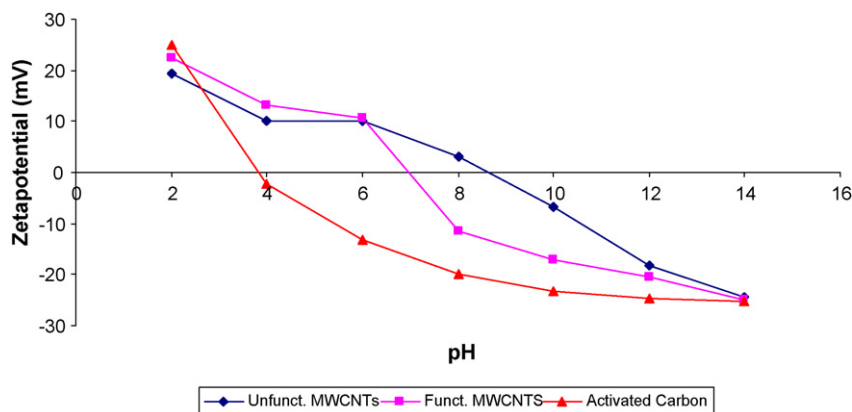


Fig. 4. The zeta potential curves for each type of adsorbent as a function of pH.

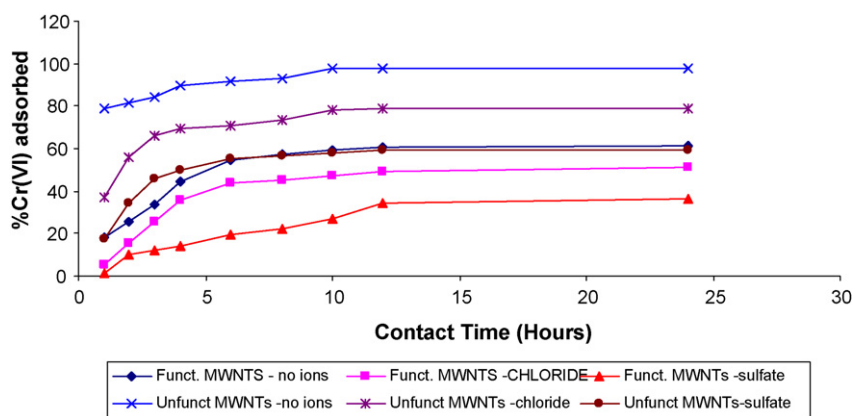


Fig. 5. The effect of competing anions on the uptake of Cr(VI) from aqueous solution.

MWCNTs. The BET surface area data revealed that the functionalised MWCNTs had a higher surface area ($130\text{ m}^2\text{ g}^{-1}$) than the unfunctionalised MWCNTs ($30\text{ m}^2\text{ g}^{-1}$). The porosity data as expected revealed that both types of MWCNTs showed little microporosity. The diffusion issues, expected with activated carbons that have a high microporosity are therefore not expected for the MWCNTs.

3.4. Initial Cr(VI) concentration

Fig. A2 shows the effect of the initial Cr(VI) concentrations on the adsorption capacities of the adsorbents. The percentage Cr(VI) adsorbed decreases as the initial Cr(VI) concentration increases where the %Cr(VI) adsorbed decreases steadily to about 15% as the initial concentrations increase to 3000 and 4000 ppb, respectively. Since the quantity of nanomaterials used was fixed at 0.1 g the number of active adsorption sites remained constant. These sites eventually become saturated with dichromate ions and therefore are unable to accommodate any more ions at higher concentrations. It is of interest to note that the unfunctionalised MWCNTs still adsorb to a greatest extent at lower concentrations. However, at higher concentrations when saturation starts to set in the adsorption capacities of both the functionalised and unfunctionalised MWCNTs are almost the same. As expected, activated carbon again showed no significant uptake of Cr(VI).

3.5. Competing anions

Competing anions are known to influence Cr(VI) uptake [46,48,56,58]. The chloride ion was selected as a possible competing anion as this ion is often added to industrial effluents for

water treatment and has already displayed a potential to hinder the adsorption of Cr(VI) on adsorbents like activated carbon [58]. The other ion that was selected was the sulphate ion. This ion is chemically similar to dichromate ion with respect to charge. Fig. 5 shows the influence of these interfering ions (0.1 M) on the uptake of Cr(VI). The adsorption of the dichromate ions is clearly hindered by the presence of potentially competitive anions. The negatively charged dichromate ions are easily repelled by the negatively charged chloride and sulphate ions.

The sulphate ion inhibits the adsorption process to a much greater extent than the chloride ions. This is possibly due to the chemical similarity between the dichromate and sulphate ions and the extra negative charge on the sulphate ion.

It is possible that the nanotube surface has a greater affinity for the chloride and sulphate ions than for the dichromate ions. Thus, a possible ion-exchange mechanism could account for the adsorption that has occurred. This is confirmed by the results shown in Fig. 6 which clearly shows that the uptake of Cr(VI) by both types of MWCNTs is hindered by the presence of both sulphate and chloride ions and these ions thus work synergistically in hindering the adsorption process. In other words, the decrease in adsorption is additive when both types of competing anions are present.

3.6. Adsorption isotherms

The Langmuir and Freundlich isotherms are the two most common isotherms that describe the distribution of a metal ion between a solid and a liquid phase and have been extensively used in the literature to model the uptake of various adsorbents [15,43,44,54,58]. The adsorption data obtained for both the functionalised and

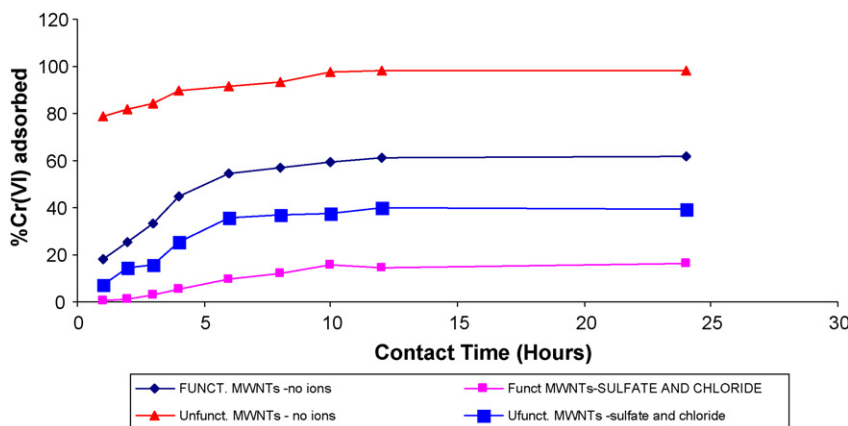


Fig. 6. The combined effect of sulfate and chloride ions on the uptake of Cr(VI).

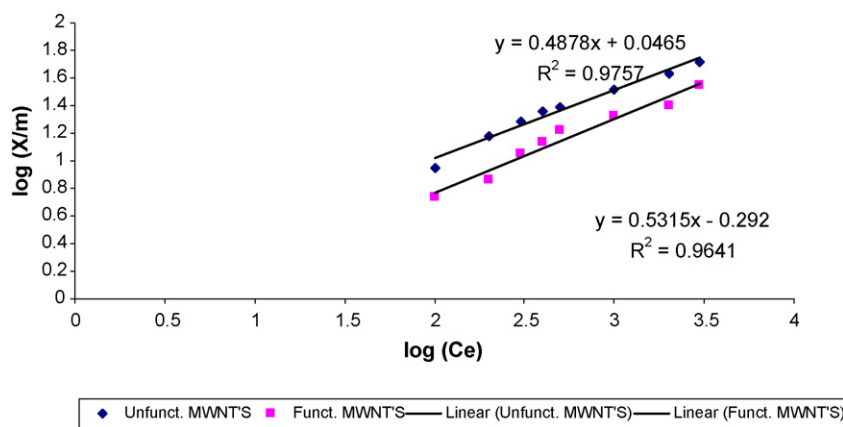


Fig. 7. The Freundlich adsorption isotherm for both functionalised and unfunctionalised MWCNTs.

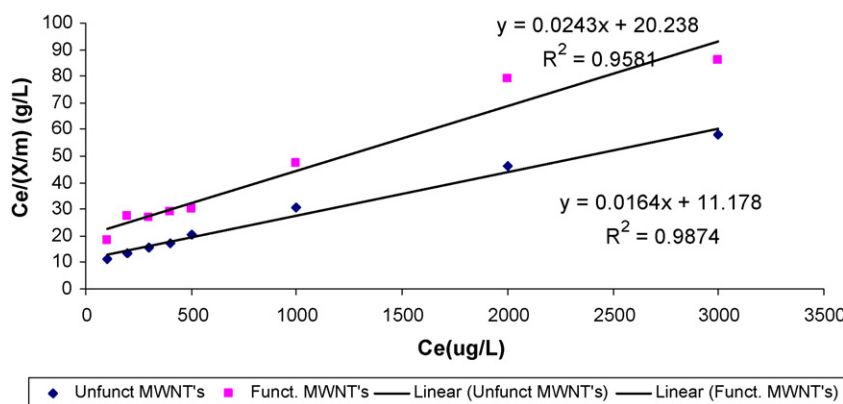


Fig. 8. The Langmuir adsorption isotherm for both functionalised and unfunctionalised MWCNTs.

unfunctionalised MWCNTs as a function of initial Cr(VI) concentrations was used to fit the linear forms of the Freundlich and Langmuir adsorption isotherms. The linear form of the Freundlich equation is given as:

$$\log\left(\frac{X}{m}\right) = \log K + \frac{1}{n} \log C_e \quad (1)$$

where X is the amount of Cr(VI) adsorbed (μg), m is the mass of adsorbent onto which Cr(VI) is adsorbed, and C_e is the equilibrium concentration of Cr(VI) in solution, K is a fitting parameter which is a constant and $1/n$ is a measure of adsorption intensity [54]. Basically this isotherm indicates that the ratio of the amount of solute adsorbed onto a given mass of adsorbent to the concentration of solute in solution varies as a function of solution concentration. Fig. 7 shows the plot of $\log(X/m)$ against $\log C_e$ for both the functionalised and unfunctionalised MWCNTs.

It can be seen from Fig. 7 that the plots obtained for both types of adsorbents are linear with R^2 values of 0.98 and 0.96 respectively. This suggests that the Freundlich Isotherm applies to both adsorbent–adsorbate systems. The $1/n$ values for the unfunctionalised and functionalised MWCNTs are calculated as 0.49 and 0.53 respectively from the data. Thus, not much difference in the adsorption intensities of both adsorbents is observed and since these values are less than 1, favourable adsorption occurs [15,43].

The data was also plotted using the linear form of the Langmuir equation:

$$\frac{C_e}{X/m} = \frac{1}{bQ} + \frac{C_e}{Q} \quad (2)$$

where C_e is the equilibrium concentration of Cr(VI) in solution, Q is the number of moles of Cr(VI) adsorbed per unit mass of adsor-

bent (adsorption capacity) upon forming the monolayer on the adsorbent surface, and b is the Langmuir constant which is related to binding energy [54]. This isotherm applies only to monolayer adsorption on a surface which contains a finite number of binding sites [54]. This is also based on the assumption that the energies of adsorption are uniform and no transmigration of adsorbate occurs in the plane of the adsorbing surface. Fig. 8 shows the plot of $C_e/(X/m)$ against C_e for both the unfunctionalised and functionalised MWCNTs. Fig. 8 shows clearly that both the functionalised and unfunctionalised MWCNTs obey the Langmuir Isotherm.

3.7. Desorption

Fig. 9 shows the plot of the % Cr(VI) desorbed against washing time. From Fig. 9 it is seen that almost all the Cr(VI) adsorbed onto the surfaces of the functionalised and unfunctionalised MWCNTs is

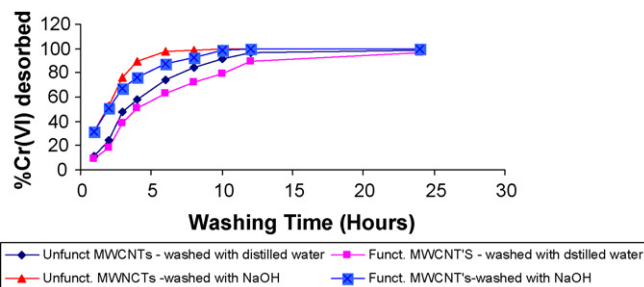


Fig. 9. The %Cr(VI) desorbed from the surface of functionalised and unfunctionalised MWCNTs.

desorbed after washing the adsorbed Cr(VI) off at hourly intervals ranging up to 24 h with 100 mL distilled water per washing. Both types of MWCNTs can therefore be regenerated and reused after desorption has occurred provided that the structural integrity of these materials is not significantly altered by the desorption process.

Further, it was found that at a higher pH (pH 14) desorption occurs to a faster extent for both types of MWCNTs. This suggests that the excess hydroxyl ions present at high pH aid in the desorption of Cr(VI) by repelling the negatively charged dichromate ions or rather by out competing these ions for active surface sites. Mungasavalli et al. [55] also made a similar observation for the uptake of Cr(VI) by the biological organism, *Aspergillus Niger*.

3.7.1. Mechanism of Cr(VI) removal

Four primary mechanisms can account for the uptake of Cr(VI) by the MWCNTs. These are an ion-exchange mechanism, electrostatic interactions, a redox mechanism and intraparticle diffusion. The redox mechanism is supported by the higher degree of adsorption that is observed at lower pH where Cr(VI) is known to be reduced to Cr(III). This can be coupled to the oxidation of the nanotube surface which will consequently contain carboxyl moieties. The Cr(III) ions generated are then adsorbed by forming bonds with the oxygen atoms on the carbonyl group (chemisorption). However, the fact that the adsorbed chromium readily desorbs rules out the possibility of this mechanism.

Adsorption is also reduced at higher pH where Cr(VI) predominates as $\text{Cr}_2\text{O}_7^{2-}$. This strongly suggests that there is competition between the excess hydroxyl ions present at higher pH and the negatively charged dichromate ions for active adsorption sites on the nanotube surfaces. This ion-exchange or chemical affinity competition is also supported by the fact that the competing anions such as chloride and sulphate ions reduce the uptake of Cr(VI). These ions are clearly out competing the dichromate ions for active adsorption sites.

An ion-exchange mechanism can be explained in terms of anion sizes. Even though the pH_{PZC} of the three adsorbents suggest that electrostatic repulsion also plays a key role, the dichromate ions are larger than the hydroxyl, chloride and sulphate ions and can thus be easily displaced from the adsorption sites. The competing anions were also present in larger concentrations than the dichromate ions (0.1 M in each case as opposed to 100 ppb dichromate) and this can also play a role in the competition process.

The n values of the adsorption isotherms also indicate that intraparticle diffusion slows down the rate of adsorption. This accounts for the equilibrium being only attained after 12 h of contact time.

Electrostatic interactions between the anions and the electron rich functional groups on the surfaces could also hinder the adsorption process to a minor extent.

4. Conclusion

The data presented in this paper has shown conclusively that both functionalised and unfunctionalised MWCNTs can adsorb ppb

levels of Cr(VI) from aqueous solution. Both adsorbents have a superior adsorption capability to that of activated carbon. The unfunctionalised MWCNTs have demonstrated a superior adsorption capability to that of the functionalised MWCNTs. This has been attributed to the fact that the functionalised MWCNTs contain electron rich atoms in their functional groups which repel the negatively charged dichromate ions and inhibit the adsorption process. This is verified by the fact that the adsorption capability of the MWCNTs improves by 30% once all the functional groups have been removed. This is further supported by the fact that the unfunctionalised MWCNTs have a higher pH_{PZC} than the functionalised MWCNTs.

The key factors which favour the adsorption process are increasing contact time, low pH and low initial concentrations of Cr(VI). The adsorption process is significantly inhibited by the presence of competing anions such as chloride and sulphate.

Both adsorbents obey the Langmuir and Freundlich Isotherms. The Langmuir Isotherm is consistent with monolayer adsorption on the MWCNTs. Both isotherms indicate that favourable adsorption occurs and that intraparticle diffusion could be a rate-limiting step resulting in the slow attainment of equilibrium.

Besides intraparticle diffusion, an ion-exchange mechanism has been identified as the key mechanism governing the adsorption process. This is supported by the fact that the adsorption process is enhanced at low pH and hindered by the presence of competing anions.

The dichromate ions are easily desorbed from the surfaces of both types of MWCNTs. The desorption is also enhanced at high pH due to the fact that the dichromate ions are deprotonated at high pH and are easily repelled and out competed by the excess hydroxyl ions. Thus both adsorbents can be regenerated and reused to reduce cost factors. However, the desorption must be carefully conducted where the adsorbed chromium must be retained on the solid surface at low pH until this can be released back into aqueous solution for recycle and reuse.

Unfunctionalised MWCNTs have proven to be excellent adsorbents for the effective removal of parts per billion levels of Cr(VI) from aqueous solution. It is now of interest to see whether these MWCNTs can be used on actual industrial effluents containing ppb levels of Cr(VI). Such a study has already been initiated and will be communicated in our next paper.

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Appendix A

Figs. A1 and A2

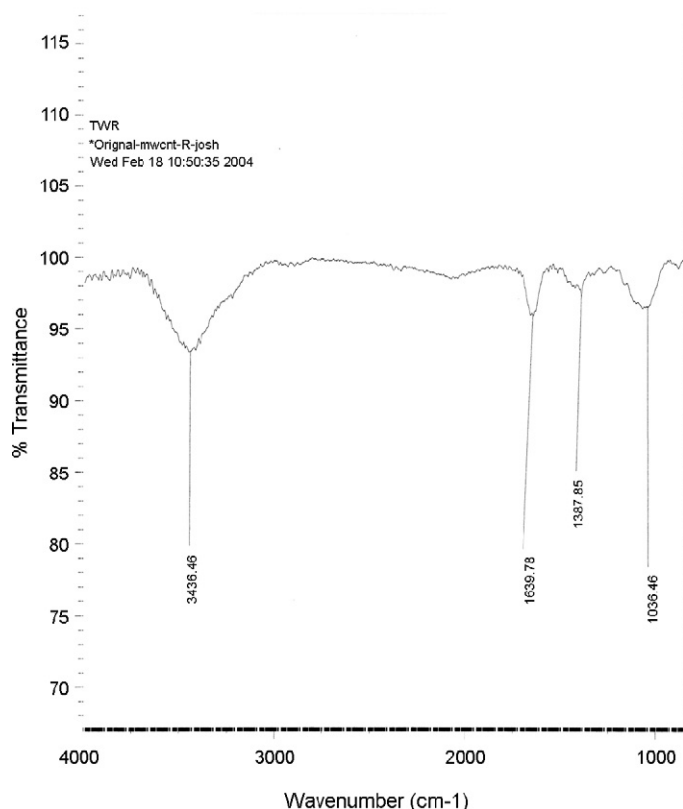


Fig. A1. The IR spectrum of the functionalised MWCNTs.

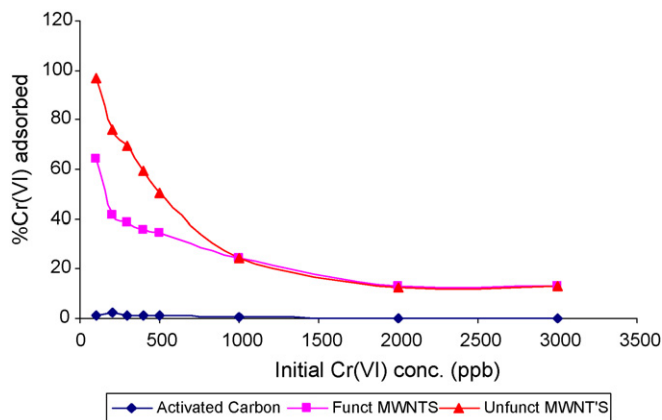


Fig. A2. The effect of initial Cr(VI) concentrations on the uptake of Cr(VI) by the various adsorbents.

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