



## The defluoridation of drinking water using multi-walled carbon nanotubes

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### ABSTRACT

In this study, the potential sorption capacity of multi-walled carbon nanotubes (MWCNTs) was investigated as a means of removing fluoride from the drinking water of a number of regions in Iran and from experimental solutions. The test was conducted in both batch and continuous operation modes. Batch mode experiments were used to study the effect of parameters such as pH, contact time, ionic strength, adsorbent dose, adsorbent capacity, and the presence of foreign anions on the efficiency of fluoride removal. The results showed that the highest level of sorption occurs at pH 5 (about 94% at 18 min). The ionic strength of the solutions and the presence of co-anions such as chloride, nitrate, sulfate, hydrogen carbonate, perchlorate had a negligible effect on the sorption of  $F^-$  onto MWCNTs. Sorption capacity measurements revealed that MWCNTs have a saturation capacity of 3.5 mg of  $F^-$  per gram. Sorption data were best fitted with the Fruendlich sorption isotherm equation, which indicates that  $F^-$  tends to be adsorbed on MWCNTs in a multilayered manner. Experiments using Kohbanan city drinking water, which contains the highest level of  $F^-$  among the drinking water samples studied, showed that MWCNTs can remove over 85% of fluoride content.

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## 1. Introduction

Pure drinking water is available to only a small percentage of the human population, while the rest consume relatively impure water. Impurities may be introduced into the water either by natural sources or by industrial wastewater. Fluoride is an essential microelement for animals and human that its intake in the proper extent protects teeth against caries especially in childhood [1], but excessive exposure to fluoride has detrimental effects on bones and teeth (dental caries) and long-term exposure at higher concentrations can lead to tooth and bone poisoning [2]. However the minimum nutritional requirement of fluoride is not determined exactly until now, but the risk of adverse effects on skeleton may be increased at total fluoride intakes above 6 mg/day and at fluoride intake of 14 mg/day, clear adverse skeletal effects may be observed. Fluoride can be absorbed by human body via food, drinking water, toothpaste, mouthwash products and air, but air is not usually a major source of uptake [1,3,4]. Drinking water is the main source of fluoride and in some areas is one of the most abundant pollutants in underground water sources and is a major obstacle to the supply of pure drinking water. Fluoride is more toxic than lead but less toxic than arsenic, and it is considered an

accumulative toxin. According to World Health Organization (WHO) standards [5], the acceptable concentration of fluoride in drinking water is 0.5–1 mg/L, and the maximum acceptable concentration is 1.5 mg/L [2,6,7]. Therefore, defluoridation of drinking water is necessary, especially in hot and dry climates, where people drink more water.

Various methods have been proposed for water defluoridation, such as the precipitation method, which involves adding chemical agents and segregating insoluble compounds; the sorption technique, which uses adsorbents like chemically activated carbon (AC) [8], natural zeolites [9] and cuttlefish bones [10]; membranous methods, such as electrodialysis [11], Donnan dialysis [12], reverse osmosis [13], ion exchange [14], electrolysis [15] and nanofiltration [16]; and a method that combines electroflootation and electrocoagulation [17]. Among these techniques, adsorption seems to be an effective, environmentally friendly and economical one [18,19]. Adsorption by carbon based materials such as carbon nanotubes which is essentially a sheet of graphite that has been rolled into a tubular form may be accomplished. Carbon nanotubes are increasingly recognized for their sorption capabilities, which result mainly from their extremely small size, uniform pore distribution and large specific surface area. It has also been shown that their well-defined porosity and functionality make them superior to other adsorbents, like AC [20].

This study aims to investigate the efficiency of MWCNTs in drinking water defluoridation. A comparative study using AC and fullerene as adsorbents was also undertaken. The effects of contact

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time, initial pH of the solution, initial  $F^-$  concentration, and the presence of competing anions on the defluoridation of drinking water were investigated.

## 2. Materials and methods

### 2.1. Materials

In this study, MWCNTs and Fullerene C60 produced by PlasmaChem<sup>®</sup> GmbH, Germany, were utilized. The purity of MWCNTs was higher than 95%, and the diameter and length of the MWCNTs were 10–30 nm and 1–10  $\mu$ m, respectively. There were 3–15 walls per MWCNT. Powdered AC was commercially obtained from E. Merck AG (Darmstadt, Germany). In all experiments ultrapure water (UPW) used for the preparation of solutions and dilutions was produced by a Milli-Q system (18.2 M, Millipore, Bedford, MA, USA). All fluoride solutions were prepared in polyethylene plastic containers. A 100 mg/L stock solution of  $F^-$  was prepared by dissolving 0.022 g of NaF in 100.0 mL of UPW. 50 mL standard solutions of 0.05, 0.1, 0.5, 1.0, and 2.0 mg/L were prepared by dilution of the stock solution with UPW and TISAB (Total Ionic Strength Adjusting Buffer). The fluoride samples and the fluoride standard solutions were diluted 1:1 with TISAB. The buffer solution was prepared [21,22] by dissolving 58.0 g of NaCl and 57.0 mL of glacial acetic acid in UPW adjusted to pH 5.5, then diluted to 500.0 mL in a volumetric flask. Solutions of 0.1 M HCl and 0.1 M NaOH were used to adjust the pH. Nitric acid, hydrochloric acid, sodium sulfate, sodium bicarbonate, sodium nitrate, sodium hydroxide, and sodium perchlorate were used to study the effect of co-anions on the sorption of fluoride. All the chemicals used in this study were purchased from E. Merck AG (Darmstadt, Germany) and used as received.

### 2.2. Optimization and validation of the potentiometric method

To determine the fluoride concentration a fluoride specific electrode (PF-1; Shanghai Precision Scientific Instrument Co., Ltd., Shanghai, China) and a calomel reference electrode (232; Shanghai Precision Scientific Instrument Co., Ltd., Shanghai, China) connected to a Metrohm 692 pH/Ion Meter (Metrohm Ltd., Switzerland) was used. The potentiometric method was studied at pHs ranging from 2 to 8 and validated in relation to precision, accuracy, linearity, as well as limits of detection and quantitation. The FISE was calibrated using five NaF solutions (obtained from the stock solution) of concentrations ranging from 0.05 mg/L to 2 mg/L (a range in which the electrode exhibits true Nernstian behavior).

### 2.3. Sorption experiments

Fullerene C60, MWCNTs, and AC were used as adsorbents. Sorption was studied using batch and continuous methods. All the experiments for fluoride determination were carried out using fluoride solutions containing TISAB. In all sorption experiments, the samples that were in contact with the adsorbents after filtering (in batch experiments) and eluents (in continuous experiments) were adjusted to pH 5.5 before measurement by FISE.

### 2.4. Batch sorption experiment

In batch sorption experiments, 0.05 g of each adsorbent was weighed out and placed in contact with 10 mL of the 10 mg/L  $F^-$  solution in TISAB. The adsorbents were placed in contact with the  $F^-$  solution for periods ranging from 0 to 22 min in 2-min intervals. The contact between the adsorbent and the  $F^-$  solution was facilitated by agitation on a shaker. After each specified contact time, the solution potential was directly measured. The removal

efficiency was calculated using the expression  $(([F^-]_{\text{init}} - [F^-]_{\text{fin}})/[F^-]_{\text{init}})$ , where  $[F^-]_{\text{init}}$  and  $[F^-]_{\text{fin}}$  are the initial and final fluoride concentrations, respectively. The amounts of adsorbed  $F^-$  per unit weight of adsorbent ( $F_{\text{ad}}$ ) were determined as the ratio of  $F^-$  sorption to the total weight of solid.

### 2.5. Continuous sorption experiment

In the continuous sorption experiment, a 5 mL syringe with an inner diameter of 10 mm and a length of 90 mm was used. Two filters were placed in the syringe outlet. Prior to running the experiment, the cartridge was filled with 0.1 g of each adsorbent, which was first conditioned by passing ethyl alcohol and deionized water through the cartridge. At this stage, 10 mL of the 10 mg/L  $F^-$  solution was passed through the conditioned cartridge. The solution potential was measured before and after passing the solution through the cartridge.

### 2.6. Effect of pH on the sorption process

To evaluate the effect of pH on  $F^-$  sorption in the batch experiments, the initial pH of the fluoride solutions was adjusted to 5.0, 7.0, and 9.0.

### 2.7. Effect of co-anions on the sorption of $F^-$

To investigate the effects of chloride, nitrate, sulfate, and hydrogen carbonate and their concentrations on fluoride sorption, the mixed solutions containing fluoride and each of the aforementioned anions at various final concentrations of 1, 50, and 100 mg/L were treated in the batch system. In addition, perchlorate solutions at 0.002, 0.1, and 0.2 M were studied.

### 2.8. Defluoridation capacity measurements

The continuous system was used to assess the defluoridation capacity. For this purpose, two adsorbent doses of 0.05 and 0.1 g of MWCNTs were used. In each experiment, 10 mL portions of 10 mg/L fluoride solutions were passed through the column until the sorbent was saturated. The total amount of fluoride removed by the sorbent (mg) divided by adsorbent mass (g) was used to calculate defluoridation capacity.

### 2.9. Sorption isotherm

The sorption data were fitted to the Langmuir, Freundlich, and Dubinin–Radushkevitch (D–R) equations to find the sorption isotherm of fluoride removal by MWCNTs. The batch system data were used for this adaptation.

## 3. Results and discussion

### 3.1. Potentiometric FISE method optimization

To determine the fluoride concentration, the potentiometric method was optimized in relation to pH. The potential measurements of a 0.2 mg/L solution at different pHs are shown in Fig. 1.

As can be seen in Fig. 1, increasing the pH of the fluoride solution decreases the measured potential. According to the Nernst equation ( $E = L - 0.0591 \log a_{F^-}$ ), this is due to the greater activity of the fluoride ion. Also, fluoride activity does not change considerably at pHs higher than 5. Because the acceptable pH of drinking water is between 5 and 8.5, pH 5.5 was used in all of the following experiments. The potentiometric method with FISE demonstrated a linear behavior ranging from 0.05 mg/L to 2 mg/L ( $E = 60.601C + 36.328$ ,  $r = 0.9999$ ,  $n = 3$ ), and the RSD% of the three

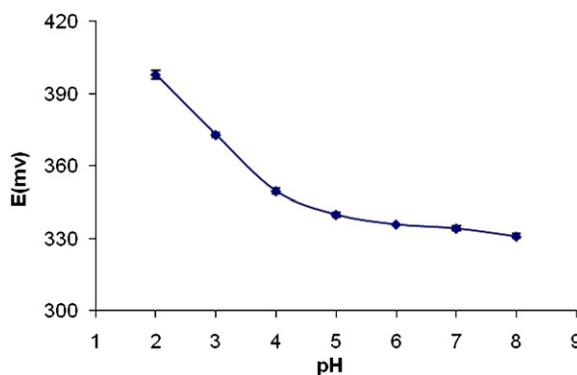


Fig. 1. Effect of fluoride solution (0.2 mg/L) pH on potential measured by FISE.

repetitions for each concentration was lower than 4.4%. The relative error percentage was less than 3.3%, the detection limit was 0.09 mg/L, and the quantitation limit was 0.16 mg/L. An important issue regarding the determination of sorption of fluoride ion on MWCNTs is to evaluate fluoride ion concentration reliably. Ionic strength of the solutions containing fluoride ion has a considerable effect on the potential reading. In order to have an acceptable relationship between fluoride ion concentration and its activity, TISAB must be used to prevent changing of ionic strength of the solutions followed by changing fluoride ion concentration. In this study, since UPW was used for the preparation of standard solutions, ionic species like iron and aluminum were not detectable, and since fluoride concentrations after sorption on MWCNTs were lower than 0.4 ppm, low level TISAB could be sufficient to adjust the ionic strength of the solution and its changes were insignificant (less than 0.4%) and ionic strengths of the fluoride standard solutions were less than 0.707 M, whereas addition of ions to study the interference of co-anions on fluoride sorption may change ionic strength to amount of 0.710 M which is about 0.43% greater than standard fluoride solutions. Because Debye–Hückel equation for determination of activity coefficient is not applicable at this high ionic strengths, it is impossible to define precisely the effect of 22% increase of ionic strength on fluoride activity, but in ionic strengths lower than 0.1 that Debye–Hückel equation can be used in activity coefficient determination, calculations showed that even 23% increase in ionic strength, may lower activity coefficient of fluoride just for 2.3%.

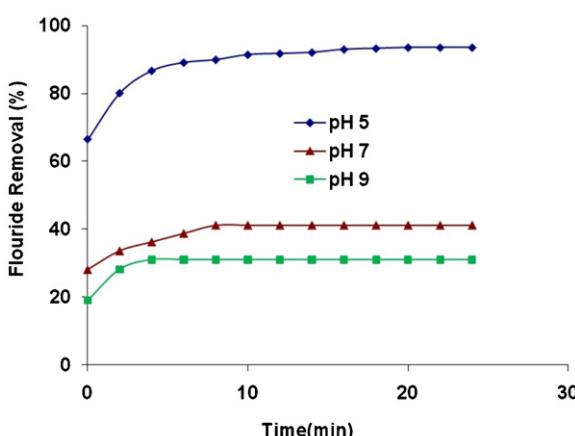


Fig. 2. Adsorption profiles of fluoride by MWCNTs at different pHs. Adsorbent dose is 0.05 g, and initial fluoride concentration is 10.0 mg/L.

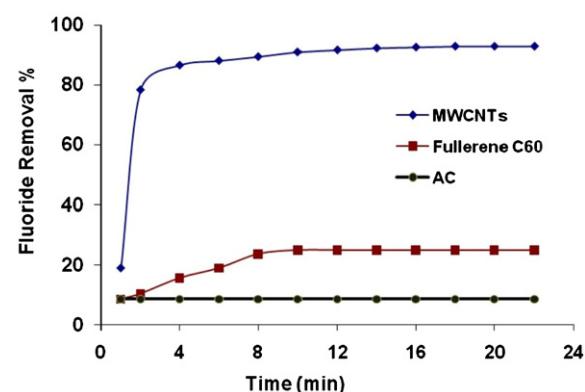


Fig. 3. Adsorption profiles of fluoride by various adsorbents.

### 3.2. Sorption method

The effect of pH on fluoride removal was studied at pHs ranging from 5.0 to 9.0, and the results are shown in Fig. 2.

pH plays a major role in fluoride sorption on MWCNTs. The maximum sorption of fluoride was 93.5% at pH 5.0, and at higher pHs, the sorption capacity decreased significantly, reaching 41.2% at pH 9. This is consistent with the results obtained for other adsorbent systems [23]. The sharp reduction in the amount of fluoride adsorbed in the alkaline pH range can be attributed to the competition for sorption sites between hydroxyl ions and fluoride [24].

### 3.3. Effect of contact time and the type of adsorbent

The sorption of fluoride on MWCNTs, fullerene C60 and AC was studied. The sorption results are shown in Fig. 3.

Fig. 3 shows that the sorption of fluoride on MWCNTs reached 19% of the fluoride in solution after 1 min and increased to more than 90% after 6 min, at which point it had reached equilibrium. By contrast, the sorption on AC was constant and equal to approximately 8.6%. The maximum sorption of fluoride on the fullerene adsorbent was about 25%.

The percentage of fluoride removed by MWCNTs after different contact times can be seen in Fig. 3. Although at the beginning the percentage of removed fluoride increased with longer contact times, it approached a plateau after a few minutes. Presumably, the equilibrium time is the time at which the curves appear almost

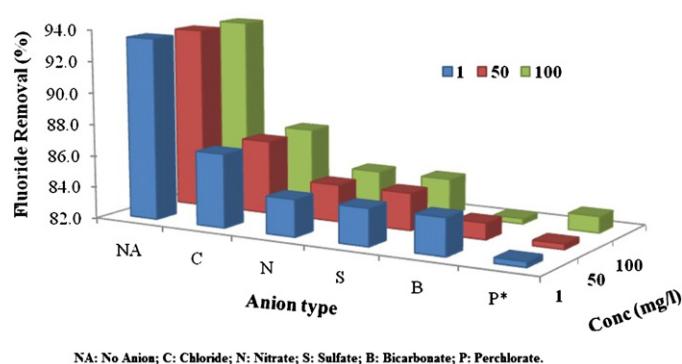


Fig. 4. Effect of some co-anions at different concentrations on fluoride removal by MWCNTs.

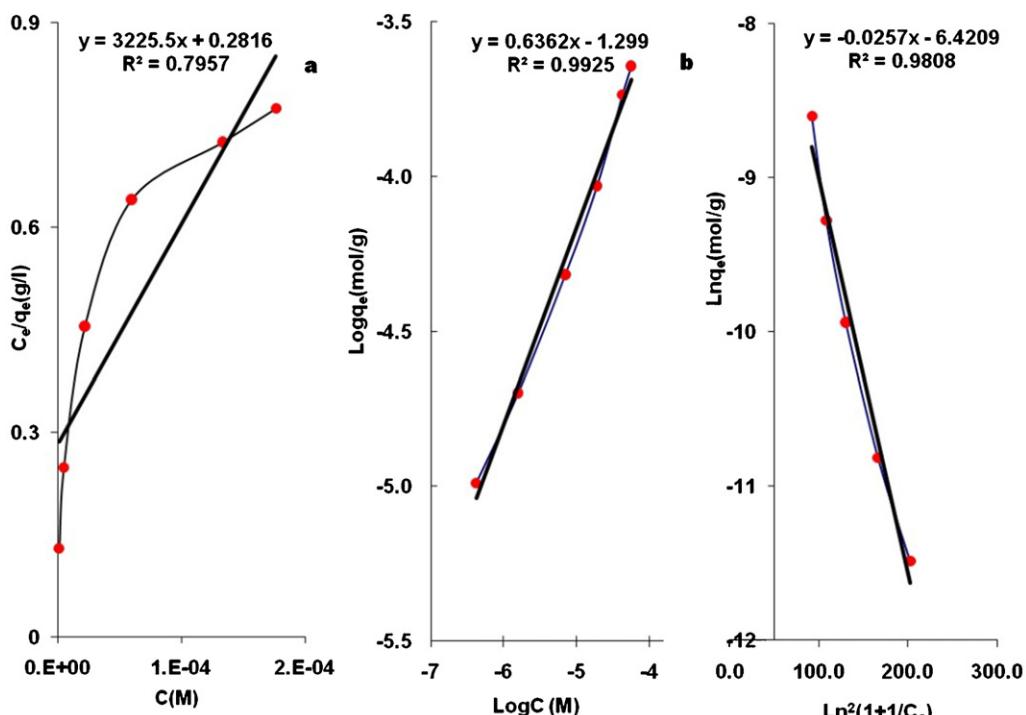


Fig. 5. Langmuir (a), Freundlich (b), and D-R (c) fitting of adsorption isotherms of fluoride on MWCNTs.

asymptotic to the time axis. In this case, the equilibrium was reached at 18 min; the sorption percentage changed from 86% at 4 min to 93% at 18 min, at which point it plateaued. Compared to the equilibrium time reported by other researchers [3], this represents a 50–70% decrease.

### 3.4. Effect of other co-anions

In addition to fluoride ions, drinking water contains other anions, such as chloride, nitrate, sulfate, hydrogen carbonate and perchlorate. The impact of other anions on the efficiency of fluoride ion removal by MWCNTs is shown in Fig. 4.

The percentage of fluoride removed by MWCNTs is at least 82%, even in the presence of a high concentration of anions. As depicted in Fig. 4, conjugate bases of strong mineral acids have the smallest influence on fluoride sorption. Chloride anion interferes the least, while bicarbonate anion interferes the most. This can be explained by the fact that conjugate bases of weak acids produce more hydroxyl ions, which compete with fluoride for sorption sites. Higher initial concentrations of bicarbonate decreased the efficiency of fluoride removal more than did higher initial concentrations of other anions. Due to the use of perchlorine as a drinking water disinfectant, perchlorate anions may also be present in water. The presence of perchlorate anions did not significantly interfere with fluoride removal. Though the sodium perchlorate concentration ranged from 0.002 M to 0.2 M, the efficiency of fluoride removal was still greater than 83%.

### 3.5. Sorption isotherm

A number of previous studies have shown that the Langmuir, Freundlich and D-R isotherms can be used to simulate the sorption of fluoride on MWCNTs [25,26]. To model the sorption equilibrium data, three widely used isotherms, the theoretical Langmuir isotherm, empirical Freundlich isotherm, and D-R isotherm, were

examined. The Langmuir isotherm, which is regarded as the most applicable isotherm, is commonly applied in solid/liquid systems to describe saturated monolayer sorption [17]. The linearized form of the Langmuir equation is the following:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m}$$

where  $C_e$  is the equilibrium concentration (mg/L);  $q_e$  is the amount of ion adsorbed (mg/g);  $q_m$  is  $q_e$  for a complete monolayer (mg/g);  $K_a$  is the sorption equilibrium constant (L/mg).

The Freundlich isotherm [27], which is based on sorption on a heterogeneous surface, is the earliest known relationship that describes sorption equilibrium. Its linearized form is given as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

where  $K_F$  and  $1/n$  are the empirical constants that represent the sorption capacity and sorption intensity, respectively.

The D-R isotherm model is valid at low concentration ranges and can be used to describe sorption onto both homogeneous and heterogeneous surfaces [28]. The D-R equation has a general linearized expression:

$$\ln q_e = \ln q_m - \beta \epsilon^2$$

where  $\beta$  is the activity coefficient related to mean sorption energy ( $\text{mol}^2/\text{kJ}^2$ ), and  $\epsilon$  is the Polanyi potential. The sorption isotherms of fluoride on MWCNTs based upon these three models are shown in Fig. 5.

The relative values calculated from the three models are listed in Table 1.

**Table 1**

Langmuir, Freundlich, and D-R isotherm constants for the adsorption of fluoride on MWCNTs at ambient temperature.

Model	Parameter		R
Langmuir	$q_m$	$K_a$	
	$3.10 \times 10^{-4}$	$1.15 \times 10^4$	0.892
Model	Parameter		R
Freundlich	$n$	$K_F$	
	1.57	$5.02 \times 10^{-2}$	0.996
Model	Parameter		R
D-R	$q_m$	$\beta$	
	$1.63 \times 10^{-3}$	0.025	0.990

**Table 2**

Fluoride concentration of real drinking water at different parts of Iran, and percent of fluoride removed by MWCNTs in each sample.

City	Fluoride conc. in water (mg/L)	Fluoride adsorbed (%)
Kerman	0.2	78.9
Mashad	0.3	76.8
Tehran	0.2	77.6
Esfahan	0.2	71.8
Gorgan	0.3	76.1
Yazd	0.2	72.9
Bandarabas	0.2	75.5
Rafsanjan	0.3	74.9
Bam	0.3	77.2
Kohbaban	1.2	83.3

The Freundlich and D-R models simulate the experimental data more accurately than the Langmuir model.

### 3.6. Fluoride removal from real drinking water

Drinking water was obtained from various parts of Iran. First, the fluoride content of these samples was determined, and then it was removed by MWCNTs. Results are shown in Table 2.

Results show that the fluoride concentration of drinking water in most Iranian regions is in the acceptable range, with the exception of the city of Kohbaban in the Kerman province, where the concentration of fluoride exceeds the acceptable limit. In all cases, MWCNTs were able to remove more than 70% of fluoride. After the water was passed through the adsorbent, its fluoride content fell to an acceptable level.

### 4. Conclusions

In this study, MWCNTs were used to remove fluoride from both experimental solutions and natural drinking water for the first time. The main conclusions are as follows:

1. The performance of the MWCNTs is excellent because it can remove fluoride even at low concentrations, i.e., less than 2 mg/L. Therefore, it may be more efficient than other reported adsorbents, which do not have an effect on fluoride concentrations lower than 2 mg/L.
2. Fluoride removal was highly dependent on the pH of the solutions, the type of adsorbent, and the contact time.
3. The presence of co-anions had no effect on the sorption of fluoride by MWCNTs.
4. The equilibrium sorption data were fitted reasonably well to the Freundlich isotherm model.
5. This method could be utilized routinely to remove fluoride from drinking water.

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