Adsorption of fluoride from water by aligned carbon nanotubes

Yan-Hui Li^{a,*}, Shuguang Wang^b, Xianfeng Zhang^a, Jinquan Wei^a,
Cailu Xu^a, Zhaokun Luan^b, Dehai Wu^a

^a*Department of Mechanical Engineering, Tsinghua University, Beijing 100084, PR China*

^b*State Key Laboratory of Environmental Aquatic Chemistry, Research Center for
Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, PR China*

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Abstract

Aligned carbon nanotubes (ACNTs), a new type of carbon material, were prepared by catalytic decomposition of xylene using ferrocene as catalyst. The kinetics experiment of ACNTs shows that fluoride adsorption rate is fast in the first 60 min and the adsorption capacity reaches 3.0 mg/g rapidly, then it decreases and adsorption achieves equilibrium gradually in about 180 min. The fluoride adsorption of ACNTs depends slightly on the solution pH value. The highest adsorption capacity of ACNTs occurs at pH 7 and reaches 4.5 mg/g at equilibrium fluoride concentration of 15 mg/l. The experimental results indicate that ACNTs are promising candidate materials for fluoride removal.

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1. Introduction

The chronic toxic effects on human health of excessive intake of fluoride have been studied intensively and the fluoride concentration in the range 0.5–1.5 mg/l [1] is generally considered to be beneficial to human being. Long-term drinking water containing higher fluoride concentration than 1.5 mg/l will lead to fluorosis, which is a chronic disease characterized by mottling of teeth and softening of bones, ossification of tendons and ligaments. With the rapid development of various industries, such as semiconductor manufacturing, glass and ceramic production, uranium refinement, electroplating, etc. increasing amount of wastewater containing fluorides is being discharged. So it is imperative and significant for removing excessive fluorides from water.

* Corresponding author. Tel.: +86-10-62782413; fax: +86-10-62782413.

E-mail address: liyanhui99@mails.tsinghua.edu.cn (Y.-H. Li).

Nomenclature

C	Fluoride concentration at equilibrium (mg/l)
C_i	Initial fluoride concentration of fluoride (mg/l)
K	Parameter of the Langmuir isotherm (l/mg)
k	Parameter of the Freundlich isotherm ($l^n/\text{mg}^{1-n} \text{ g}$)
n	Parameter of the Freundlich isotherm
N	Number of experimental data points
q	Mass of fluoride adsorption at equilibrium (mg/g)
q_m	Parameter of the Langmuir isotherm (mg/g)
$q_{i,\text{exp}}$	Experimental data of mass of fluoride adsorption (mg/g)
$q_{i,\text{cal}}$	Calculated data of mass of fluoride adsorption (mg/g)
W	Mass of the adsorbent (g)
V	Volume of solution (l)

Many methods have been developed for fluoride removal from water, such as adsorption [2], ion exchange, electrodialysis [3], and precipitation [4]. Among these methods, adsorption is a widely used method for defluoridation which depends on ions (adsorbate) in fluid diffusing to the surface of a solid (adsorbent), where they bond with the solid surface or are held there by weak intermolecular forces [5]. Different fluoride adsorbents, such as activated alumina [6], fly ash [7], bone charcoal [8], spent catalysts [9], La(III) and Y(III)-impregnated alumina [10], and aluminum-impregnated carbon [11], have been investigated and have shown that large surface area and physicochemical interaction between adsorbate and adsorbent were important factors effecting fluoride adsorption from water.

Carbon nanotubes are needlelike cylindrical tubules of concentric graphitic carbon capped by fullerene-like hemispheres. Since their discovery [12], great efforts have focused on synthesis, characterization, theoretical investigation, and applications of carbon nanotubes. Their perceived novel mechanical and electronic properties, large specific area and high thermal stability indicate their tremendous potential for future engineering applications, such as hydrogen storage [13], field emission [14], catalyst supports [15], and composite materials [16], etc. Especially, as environment pollution is becoming serious, carbon nanotubes may be a promising absorbent material substituted for activated carbon in many ways. Recently Long et al. reported that carbon nanotube has better adsorption capacity for dioxin removal than that of activated carbon [17]. Our previous work [18] suggested that carbon nanotubes show high efficiency for Pb^{2+} removal after oxidation treatment with nitric acid.

Here we studied the kinetic adsorption characterization of aligned carbon nanotubes (ACNTs) and pH effect on their fluoride adsorption capacity. By comparing with activated carbon and other fluoride adsorbents, we found that ACNTs have higher fluoride adsorption capacity and great potential application in fluoride removal from drinking water.

2. Experimental

ACNTs were prepared by catalytic decomposition of hydrocarbon as described elsewhere [19]. In brief, H_2 (150 sccm) and Ar (1000 sccm) were flown in the quartz tube which contained plain quartz

glass sheets when temperature reached 800 °C, at the same time, catalyst precursor and carbon source composed by dissolving ferrocene into xylene were introduced into quartz tube using a syringe pump drop by drop at a constant time interval of 2 min. The ACNTs were observed by scanning electron microscope (SEM) and high-resolution transmission electron microscope (HRTEM).

The physical properties of ACNTs were characterized by N₂ adsorption with an ASAP 2000 Micromeritics at 77 K. Determination of the surface charge of ACNTs was carried out using a Malvern zetameter, model Zetasizer 2000.

Batch sorption experiments were carried out to investigate the pH effect on the fluoride adsorption by ACNTs. The fluoride solution used was prepared by dissolving NaF in deionized water. The adsorption experiments were carried out in glass tubes at room temperature by putting 0.05 g ACNTs in 100 ml NaF solution. After the suspension pH was adjusted with 0.1 M HNO₃ or 0.1 M NaOH solutions, the tubes were placed on a shaker (HZQ-C) and shaken for 12 h. The suspension was filtered through 0.45 µm membrane filter. The filtrate was measured by a fluoride ion spectrophotometer. The amount of fluoride adsorbed on the ACNTs was determined as the difference between initial and final concentration at equilibrium by following equation

$$q = \frac{(C_i - C)V}{W}. \quad (1)$$

3. Results and discussion

3.1. Characterization of ACNTs

Fig. 1a shows that the carbon nanotube alignment is uniform and their lengths are about 200 µm. Fig. 1b indicates that carbon naotubes align densely and their diameters range from 20 to 80 nm. The inner concentric graphite cylinders of nanotubes crystallize well, while the outer parts cover with much amorphous and microcrystalline carbon as shown by arrow in Fig. 1c. The specific area, pore volume and mean pore diameter of ACNTs are 74 m²/g, 0.15 cm³/g and 3.8 nm, respectively.

3.2. Kinetics of adsorption

The kinetics of fluoride adsorption from water was carried out by adding 1 g ACNTs into 2000 ml solution with F[−] concentration 20 mg/l without any pH adjustment (pH 6.86) and the results were shown in Fig. 2. It can be seen that the adsorption rate is fast in the first 60 min and the adsorption capacity of ACNTs reaches 3 mg/g. With further increase in time, the adsorption rate decreases and fluoride adsorption by ACNTs achieves equilibrium gradually at about 180 min and the final adsorption capacity reaches 4.2 mg/g. The kinetics curve of fluoride adsorption indicates that not only the surfaces of ACNTs can absorb the fluorine ions, but also the inner cavities of ACNTs are accessible for fluorine ions to diffuse. This is supported on the shape of the curve in Fig. 2. The former rapid adsorption may be due to the fluoride ions adsorbed on the surfaces of ACNTs directly and the latter slow adsorption mainly attributes to long-range diffusion of fluoride ions in the inner cavities of ACNTs.

Fig. 1. SEM images and HRTEM of ACNTs. (a) Low magnification, (b) high magnification, (c) HRTEM image of a single carbon nanotube.

Fig. 2. Fluoride adsorption rate of ACNTs (initial fluoride concentration 20 mg/l and 25 °C).

3.3. Adsorption isotherm

The adsorption isotherms of fluoride adsorption by carbon nanotube at different pH values are illustrated in Fig. 3. All batch experimental data were fitted to the isotherm models of Langmuir and Freundlich using a method of least squares based on an optimization algorithm. These models are represented mathematically as follows:

$$q = \frac{q_m KC}{1 + KC}, \quad (2)$$

$$q = kC^n. \quad (3)$$

Fig. 3. Adsorption isotherms of ACNTs as a function of pH values (at 25 °C).

Table 1

Freundlich isotherm parameters for fluoride adsorption by aligned carbon nanotubes

pH	k	n	Average percent deviation (%)	Correlative coefficient, R^2
3.0	0.62	0.61	21	0.94
5.0	1.46	0.45	15	0.97
7.0	1.54	0.47	19	0.96
9.0	1.31	0.53	13	0.95
11.0	1.12	0.46	11	0.97

The parameter values for these isotherms depend on the nature of the solvent–solute–adsorbent interactions. The best isotherm model is determined by the lowest average absolute percent deviation, which the equation is defined as follows:

$$\%D = \frac{1}{N} \sum_{i=1}^N \left| \frac{q_{i,\text{exp}} - q_{i,\text{cal}}}{q_{i,\text{exp}}} \right| \times 100\% \quad (4)$$

Tables 1 and 2 present the parameter values of the Freundlich and Langmuir isotherm. It can be seen that the Freundlich model provided better fits of the experimental data, with an average absolute percent deviation below 21% and the lowest correlative coefficient of 0.94, than the Langmuir model with the lowest average absolute percent deviation 19% and the large varying range of correlative coefficient. So the experimental data in this paper are characterized by the Freundlich isotherm.

3.4. Electrophoretic studies and effect of solution pH on fluoride adsorption by ACNTs

The pH value at which the zeta potential equals to zero is called the isoelectric point (IEP) and it is used to assess the adsorbent surface charge qualitatively. The IEP of ACNTs is 7.4 at ionic strength of $I = 0.02$ M. At $\text{pH} < \text{IEP}$, the ACNTs surface is positively charged and is accessible for anions, at $\text{pH} = \text{IEP}$, the surface is neutral and at $\text{pH} > \text{IEP}$, the surface is negatively charged and will repulse the anions. According to this theory, the fluoride adsorption capacity will decrease sharply as the solution pH is larger than the IEP [20]. But from Fig. 3, it can be seen that adsorption capacity of the ACNTs is good in broad pH range from 3 to 9 and depends slightly on the solution pH. The highest adsorption capacity of ACNTs occurs at pH 7 and reaches 4.5 mg/g at equilibrium fluoride concentration of 15 mg/l.

Table 2

Langmuir isotherm parameters for fluoride adsorption by aligned carbon nanotubes

pH	K	q_m	Average percent deviation (%)	Correlative coefficient, R^2
3.0	0.61	2.12	31	0.97
5.0	1.99	2.85	40	0.95
7.0	5.56	1.99	23	0.77
9.0	1.75	2.51	19	0.86
11.0	2.95	1.89	33	0.92

Fig. 4. Adsorption isotherm of fluoride on ACNTs (at pH 7 and 25 °C) compared with γ -Al₂O₃, soil and activated carbon.

While at pH 11, the fluoride adsorption capacity decreases to 1.8 mg/g due to the competition of active sites on ACNTs surfaces between OH[−] and F[−]. The broad fluoride adsorption pH range of ACNTs makes it a promising adsorbent material to remove fluoride from water.

3.5. Mechanism of fluoride adsorption by ACNTs

It is known that carbon nanotubes prepared by CVD have many defects and are coated with lots of amorphous carbon. These defects and amorphous carbon can offer active sites for fluoride adsorption on the outer surfaces of ACNTs. On the other hand, the inner cavities and the micropores or mesopores composed by internanotube space between densely ACNTs may also contribute to the effective adsorption of fluoride. It is just about the unique structure of ACNTs to make them have higher fluoride adsorption capacity within a broad pH value range.

3.6. Comparison with other adsorbents

Fluoride adsorption isotherm of ACNTs was compared with activated carbon, and γ -Al₂O₃ [20] and a soil adsorbent [21]. Fig. 4 shows that γ -Al₂O₃ and ACNTs have much higher fluoride adsorption capability than that of activated carbon and soil. At low fluoride concentration (<1 mg/l), ACNTs and γ -Al₂O₃ have the same adsorption capacity. While at higher fluoride concentration the fluoride capacity of ACNTs is apparently higher than that of γ -Al₂O₃. The fluoride adsorption capacities of activated carbon, soil, γ -Al₂O₃ and ACNTs are 0.32, 0.58, 3.7 and 4.1 mg/g at equilibrium concentration of 10 mg/l. It is important to emphasize that the specific surface area and pore volume of activated carbon are 687 m²/g and 0.47 cm³/g, respectively, which are higher than that of ACNTs, but its fluoride adsorption capacity is much lower than that of ACNTs. This may be due to the unique structure of ACNTs.

Obviously the higher adsorption capacity of ACNTs makes them have great potential application in fluoride removal from water, but the cost of using ACNTs as fluoride adsorbent is still expensive and limits this adsorbent commercial utilization currently.

4. Conclusion

The Freundlich and Langmuir isotherm models were used to describe the fluoride adsorption by ACNTs at different pH and the former was found to fit with the experimental data fairly well. ACNTs express high fluoride removal efficiency in a broad pH value range and their adsorption capacity is larger than that of γ -Al₂O₃, soil and activated carbon. Their active sites on the surface caused by defects and amorphous carbon, inner cavities and internanotube space contribute to the high fluoride removal capability of ACNTs.

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