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REMOVAL OF FLUORIDE FROM WATER BY CARBON NANOTUBE SUPPORTED ALUMINA

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ABSTRACT

This paper describes a new adsorption material, carbon nanotube supported alumina, used for fluoride removal from water. The effects of calcination temperature, alumina loading and pH on fluoride removal capacity were investigated. The optimum calcination temperature for preparing the adsorbents is 450 °C and the largest adsorption capacity takes place at alumina loading of 30 wt%. The broad pH range of 6.0-9.0 with high adsorption capability suggests that carbon nanotube supported alumina have great potential applications in practice. The adsorption data at different pH were well fitted to the Freundlich isotherm. The kinetic studies show that the adsorption reaction of fluoride removal by carbon nanotube supported alumina can be described by a second order rate equation.

Keywords: Fluoride removal, adsorption, carbon nanotube supported alumina

INTRODUCTION

Wastewaters from semiconductor manufacturing, coal power plants, glass and ceramic production, uranium refinement and electroplating industries are enriched in fluoride and must be treated to achieve a suitable level of 0.5–1.0 mg l⁻¹. Ingesting water with fluoride concentrations below this level will cause dental cavities while higher than this limit can lead to skeletal abnormalities, dental fluorosis, and kidney disease [1]. Many methods have been developed to remove the excess fluoride from wastewater: precipitation with calcium and aluminum salts [2,3], adsorption by activated alumina [4], alum, charcoal [5], ion exchange and membrane processes such as reverse osmosis nanofiltration [6], electrodialysis [7] and Donnan dialysis [8]. Of these methods, adsorption is the most widely used method and exploitation of more cost-effective adsorbents for fluoride removal has been the aim of researchers.

Carbon nanotubes (CNTs) are nanometer-size cylindrical tubules curled with concentric graphene sheets. They are arousing increasing interest in many potential applications, such as field emission [9], reinforcing materials [10] and nanodevices [11] due to their high mechanical

property [12] and unique electrical property [13]. Their nanosize structure, large specific surface area, high thermal and chemical stabilities make CNTs ideal catalyst supporters or adsorbents. Planeix *et al.* first reported that in cinnamaldehyde hydrogenation Ru/CNTs had higher selectivity for cinnamyl alcohol (up to 92%) than that of Ru/Al₂O₃ catalyst (20-30%) [14]. Che *et al.* deposited Pt and Pt/Ru nanoparticles on CNT membranes and found that such catalyst-loaded membranes showed promising applications in electrocatalyzing O₂ reduction and methanol oxidation, two reactions of importance to full cell technology [15]. Long and Yang reported that CNTs had a significantly higher dioxin removal efficiency than that of activated carbon [16]. Our previous studies suggested that CNTs and carbon nanotube supported alumina (Al₂O₃/CNTs) were good fluoride adsorbents and their fluoride removal capability were superior to activated carbon [17].

In this study, we examined the effects of calcination temperature, alumina loading and pH on fluoride removal capability of Al₂O₃/CNTs. The kinetic model was used to describe the adsorption process and the mechanism of adsorption was investigated. These fundamental data will be useful for further studying the new adsorbent used in the

treatment of wastewater containing fluoride.

EXPERIMENTAL

$\text{Al}_2\text{O}_3/\text{CNTs}$ adsorbents were prepared by wetness impregnation of CNTs with appropriate amounts of aqueous solution of aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$). After drying at 100°C , the adsorbents were calcined for 2 hours at a temperature of $250\text{--}1050^\circ\text{C}$ with an interval of 200°C under a stream of nitrogen.

The structure and morphology of the samples were studied by scanning electron microscope (SEM LEO-1350) and powdered X-ray diffraction (XRD D/max-RB). The surface area was determined using BET method (Micromeritics ASAP 2000).

Fluoride stock solution (593.1 mg l^{-1}) was prepared by dissolving NaF in deionized water. The solution was further diluted to the required concentration before use.

The batch adsorption experiments were carried out in glass tubes at 25°C by putting weighted $\text{Al}_2\text{O}_3/\text{CNTs}$ in 100 ml NaF solution. The effect of heating temperature, different weight ratio and different pH values on fluoride adsorption was studied. In the experiment the initial pH values of the suspension were adjusted with 0.1 M HNO_3 or 0.1 M NaOH solutions and the final pH values were recorded. The tubes

were placed on a shaker (HZQ-C) and shaken for 6 hours and then the suspension was filtered through a $0.45\text{ }\mu\text{m}$ membrane. The filtrate was measured by ion chromatography (4500i, U. S. A. Dionex Co.). The amount of fluoride adsorbed on the $\text{Al}_2\text{O}_3/\text{CNTs}$ was determined as the difference between the initial concentration and the equilibrium concentration.

RESULTS AND DISCUSSION

Characterization of $\text{Al}_2\text{O}_3/\text{CNTs}$ by SEM and XRD

Figure 1 shows the typical morphology of the $\text{Al}_2\text{O}_3/\text{CNTs}$ materials. The Al_2O_3 and CNTs were mixed homogeneously and amalgamated into clumps. With increasing amounts of Al_2O_3 , the CNTs in the SEM images decrease due to the covering role of Al_2O_3 , while the morphologies of the $\text{Al}_2\text{O}_3/\text{CNTs}$ prepared at different temperatures have no obvious difference in SEM images.

Five adsorbents prepared at different temperatures were characterized by XRD. The diffraction patterns show that only at 1050°C are crystalline alumina ($\alpha\text{-Al}_2\text{O}_3$) peaks, presents otherwise, the diffraction patterns are well indexed to crystalline CNTs and no peaks of crystalline alumina appear which suggest that alumina is in amorphous form.

Figure 1. SEM image showing the morphology of $\text{Al}_2\text{O}_3/\text{CNTs}$ (Al_2O_3 30 wt%, 450°C).

Effect of Calcination Temperature

The effects of calcination temperature on the fluoride removal by $\text{Al}_2\text{O}_3/\text{CNTs}$ were studied at 250, 450, 650, 850 and 1050 °C, respectively, using 0.5 mg l⁻¹ of adsorbents and

6 mg l⁻¹ of fluoride (pH=6.0). The results show that the largest adsorption capacity of 9.6 mg g⁻¹ for fluoride removal by $\text{Al}_2\text{O}_3/\text{CNTs}$ is at the calcination temperature of about 450 °C (Figure 2a). Table 1 shows the porosity of pores as determined from nitrogen adsorption isotherms. The highest

Figure 2. Effect of calcination temperature (a) and Al_2O_3 loading (b) on fluoride adsorbed onto the $\text{Al}_2\text{O}_3/\text{CNTs}$.

Table 1. Porosity of $\text{Al}_2\text{O}_3/\text{CNT}$ determined by nitrogen adsorption at different temperatures (Al_2O_3 30 wt%).

Calcination temperature (°C)	250	450	650	850	1050
Surface area (m ² g ⁻¹)	85	165	128	123	119
Pore volume (cm ³ g ⁻¹)	0.025	0.176	0.273	0.309	0.277
Mean pore diameter (nm)	12.56	4.26	8.56	10.06	9.33

specific area combining with the smallest size of the pores of $\text{Al}_2\text{O}_3/\text{CNTs}$ calcined at 450°C offers the largest adsorption capacity. The decrease in amount adsorbed at other temperatures may be due to the decline in dispersion force caused by increased pore-size and decreased specific surface area [18]. It is known that $\alpha\text{-Al}_2\text{O}_3$ has lower fluoride adsorption capacity. So the morphology of Al_2O_3 supported on CNTs changed from amorphous to $\alpha\text{-Al}_2\text{O}_3$ and is another reason for the drop in adsorption capacity of $\text{Al}_2\text{O}_3/\text{CNTs}$ calcined at 1050°C .

Effect of Al_2O_3 Loading

Five adsorbents differing in Al_2O_3 loading from 0 to 50 wt% were chosen to examine the effects of Al_2O_3 loading on the fluoride adsorption capacity ($\text{pH}=6.0$) and their porosities are shown in Table 2. The pure CNTs have the largest specific surface area and the smallest pore diameter and their fluoride adsorption capacity is 2.3 mg g^{-1} . Figure 2b shows that the

adsorption capacity of adsorbents increases with increasing Al_2O_3 loading although the specific surface area decreases and reaches 9.6 mg g^{-1} at Al_2O_3 loading of 30 wt%. The adsorption capacity descends to 5 mg g^{-1} at Al_2O_3 loading of 40 wt%. When the Al_2O_3 loading attains 50 wt%, the fluoride adsorption capacity rises again. However, $\text{Al}_2\text{O}_3/\text{CNTs}$ at this loading exists as a powder rather than clumps and is not practical to use.

Effect of pH

The effect of different pH values of the solution on fluoride removal is shown in Figure 3. High adsorption capacity for fluoride removal was obtained for $\text{Al}_2\text{O}_3/\text{CNTs}$ (Al_2O_3 30 wt%, at 25°C) in the pH range 6.0–9.0. However, at pH values <6.0 and >9.0 , the fluoride adsorption capacity was found to decrease with decreasing pH, and with increasing pH, respectively.

Table 2. Porosity of $\text{Al}_2\text{O}_3/\text{CNT}$ with different Al_2O_3 loading determined by nitrogen adsorption (450°C).

Percent of Al_2O_3 supported	0	20%	30%	40%	50%
Surface area ($\text{m}^2\text{ g}^{-1}$)	178	164	165	125	97
Pore volume ($\text{cm}^3\text{ g}^{-1}$)	0.406	0.177	0.176	0.202	0.223
Mean pore diameter (nm)	3.9	4.31	4.26	6.46	5.05

Figure 3. Amount of fluoride adsorbed onto the $\text{Al}_2\text{O}_3/\text{CNTs}$ as a function of pH (calcination temperature 450°C , Al_2O_3 30 wt%, 25°C).

Adsorption Isotherms

The experimental data for fluoride removal by Al₂O₃/CNTs were adjusted using the Langmuir and Freundlich models whose linearized equations are, respectively:

$$\frac{1}{q} = \frac{1}{q_m} + \frac{1}{bq_m C_e}$$
 (i)

$$\ln q = \ln K_F + \frac{1}{n} \ln C_e$$
 (ii)

where C_e is the equilibrium fluoride concentration (mg l⁻¹), q is the amount adsorbed (mg g⁻¹) and q_m, b, K_F and n are

Langmuir and Freundlich constants, respectively. The correlation coefficients R² (Table 3) were found to be 0.60-0.96 for Langmuir model and 0.98-0.99 for Freundlich model, respectively. So the equilibrium adsorption data for different initial fluoride concentrations at different pH fit the Freundlich model better (Figure 4).

Kinetics Studies

The kinetics of fluoride adsorption were studied by varying the contact time from 1 to 530 minutes using 0.5 mg l⁻¹ of Al₂O₃/CNTs at an initial fluoride concentration of 10.3 mg l⁻¹ (Figure 5a). It is evident that the curve obtained increases quickly during the first 75 minutes and about 50 % of the fluoride was removed from water. Then the curve increases gradually. About 75 % of fluoride is adsorbed from water when the equilibrium is reached after 20 hours.

Figure 4. Linearized Freundlich isotherms for fluoride adsorption by the Al₂O₃/CNTs at different pH (●, pH=3.0; ▲, pH=5.0; □, pH=7.0; ○, pH=9.0; ■, pH=11.0). [Al₂O₃ 30 wt%, 25 °C].

Table 3. Langmuir and Freundlich isotherm constants.

pH	Langmuir			Freundlich		
	R ²	q _m	b	R ²	K _F	n
3.0	0.99	45.32	55.16	0.98	1.13	1.33
5.0	0.77	20.62	1.99	0.98	8.24	3.71
7.0	0.76	24.15	3.51	0.98	7.06	2.99
9.0	0.60	12.99	1.71	0.99	6.01	2.93
11.0	0.98	18.35	1.07	0.99	1.86	1.59

Figure 5. Kinetic study of fluoride adsorbed onto $\text{Al}_2\text{O}_3/\text{CNT}$. a.) removal efficiency versus adsorption time; b.) logarithmic plot of removal efficiency versus time.

The following equation is applied to evaluate the adsorption kinetics [19]:

$$R = k_t t^m \quad (\text{iii})$$

where R is the fluoride removal efficiency (%), t is contact time and k_t and m are constants. A linear relationship between the log of percentage of fluoride removal versus the log of time is obtained with a regression coefficient of 0.975 (Figure

5b). The values of m and k_t are 0.323 and 0.117 min^{-m} , respectively. The order of the reaction, n , is given by the following equation [19]:

$$n = m^{-1} - 1 \quad (\text{iv})$$

and a value of 2.09 n is calculated. Thus, it appears that the kinetics of fluoride removal by $\text{Al}_2\text{O}_3/\text{CNTs}$ can be approximately represented by a second order rate equation.

Adsorption Mechanism

It was reported that anion adsorption sites on alumina are aquo groups ($-M-OH_2^+$) and hydroxo groups ($-M-OH$) [20]. Fluoride ions can be adsorbed by a positively charged surface and neutral surface through the following equations:

Equations (v) and (vi) take place at the positively charged surface and adsorbed F^- through ligand exchange. When the surface is neutral, F^- can be adsorbed by an ion exchange mechanism (equation (vii)). The isoelectric point (IEP) can be used to assess the adsorbent surface charge qualitatively. The IEP of $Al_2O_3/CNTs$ is 7.5. In the region of $pH < 7.5$, the surface charge of $Al_2O_3/CNTs$ is positive, so adsorption of fluoride will abide by equations (v) and (vi). At $pH = 7.5$, the surface of $Al_2O_3/CNTs$ is neutral and the reaction will take place according to equation (vii). By $pH > 7.5$, the hydroxo groups ($-M-OH$) will gradually disappear, at the

same time, OH^- will compete with fluoride ions for available sites left on the surface of the $Al_2O_3/CNTs$ [20].

In addition, CNTs themselves are good fluoride adsorption materials [17] due to their large surface area and layered structure. The caps of CNTs can be opened up by means of ball milling and oxidation. The opened CNTs may not only transfer F^- into the interior of the $Al_2O_3/CNTs$ clumps, but also adsorb F^- (F_{radius} 0.13 nm) on their outer surfaces, inner cavities and interlayers (0.344 nm). This could be the reason for high fluoride adsorption capacity (4.8 mg g^{-1}) of $Al_2O_3/CNTs$ even at $pH = 11.0$.

CONCLUSIONS

In summary, $Al_2O_3/CNTs$ could be used as a potential adsorbent for removal of fluoride from water. The optimum calcination temperature for fluoride removal by $Al_2O_3/CNTs$ with the largest adsorption capacity of 9.6 mg g^{-1} is about 450°C , which attribute to their higher specific area and smaller pore size. With increasing Al_2O_3 loading, the highest adsorption capacity of $Al_2O_3/CNTs$ is reached at a loading of 30 wt%. All adsorption isotherms at different pH are well fitted by the Freundlich equation. The optimal pH range of 6.0-9.0 for fluoride adsorption of $Al_2O_3/CNTs$ indicates that the new adsorbent has promising applications. Kinetic studies shows that fluoride adsorption by $Al_2O_3/CNTs$ is a second order rate reaction.

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