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Short Communication

# Chromium adsorption by aligned carbon nanotubes supported ceria nanoparticles

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## Abstract

Ceria nanoparticles supported on aligned carbon nanotubes ($CeO_2$/ACNTs), a novel adsorbent for Cr(VI) from drinking water, were prepared by chemical reaction of $CeCl_3$ with NaOH in aligned carbon nanotube solution and subsequent heat treatment. The best Cr(VI) adsorption effect of $CeO_2$/ACNTs occurs at a pH range of 3.0–7.4. The largest adsorption capacity of $CeO_2$/ACNTs reaches 30.2 mg $g^{-1}$ at an equilibrium Cr(VI) concentration of 35.3 mg $l^{-1}$ at pH 7.0. The experiment results suggest that $CeO_2$/ACNTs have great potential applications in environmental protection.

*Keywords:* Aligned carbon nanotubes; Langmuir isotherm; Freundlich isotherm; Electron microscopy; Surface charge

## 1. Introduction

Chromium is one of the extremely toxic heavy metals found in various industrial wastewaters (Alves et al., 1993). Several processes have been reported to remove Cr(VI) from aqueous solutions, such as chemical precipitation, membrane filtration, ion exchange and adsorption, the latter process is a more useful method for metal removal than the other processes. The absorbents commonly recommended for Cr(VI) removal are alumina, silica (Yabe and Oliveira, 2003) and activated carbon (Selvi et al., 2001). Wasay et al. (1996a) reported that hydrous oxides of rare earth elements exhibit high-adsorption capacity for anions.

Carbon nanotubes (CNTs) are increasingly attracting interest since their discovery (Iijima, 1991). Their small sizes, large surface area, high mechanical strength and remarkable electrical conductivities indicate their tremendous potential for future engineering applications, such as hydrogen storage (Dillon et al., 1997), field emission (Wang et al., 1998), catalyst supports (Planeix et al., 1994) and composite materials (Ajayan et al., 1994), etc. Studies of CNTs using as adsorbents have also been reported extensively. Long and Yang (2001) found that CNTs were superior absorbent for dioxin removal. Our previous work (Li et al., 2002) suggested that carbon nanotubes show high efficiency for $Pb^{2+}$ removal after oxidation treatment with nitric acid. Li et al. (2001) reported that CNTs supported metal oxides such as amorphous alumina had higher fluoride adsorption capacity which was about 13.5 times higher than that of AC-300 carbon and four times higher than that of

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$Al_2O_3$. Here we used aligned carbon nanotubes (ACNTs) as supports to deposit $CeO_2$ and found that $CeO_2$/ACNTs exhibited excellent characteristics for removing Cr(VI) from drinking water.

## 2. Experiment section

ACNTs were prepared by catalytic decomposition of hydrocarbon as described elsewhere (Cao et al., 2001). Scanning electron microscopy images (Fig. 1a) show that the carbon nanotube alignment is uniform and lengths are about 200 μm and their diameters range from 20 to 80 nm. The as-prepared ACNTs were then immersed in concentrated nitric acid and hydrofluoric acid to dissolve the catalyst particles and then washed with deionized water. The dried ACNTs were ground by ball milling to break the ACNTs into short pieces and refluxed with mixed solution of nitric acid and sulfuric acid at 140 °C for 1 h to introduce functional groups, such as hydroxyl (–OH) and carboxyl (–COOH) on the surface of the ACNTs (Jia et al., 1999). Finally they were filtered with a ceramic filter until the pH value of the ACNTs solution reached 7.0.

All chemicals used were analytical grade. The ACNTs were dispersed into distilled water and agitated with a magnetic agitator. The $CeCl_3$ ($0.035\ g\ ml^{-1}$) solution was added into ACNTs solution drop by drop. After the mixture was agitated for 1 h, NaOH solution with a concentration of 0.5 wt.% was titrated into mixture until the pH value of the mixture solution reached 8.5. The mixture solution was then dried up and heated in air at 450 °C for 20 min. The nanosized ceria particles supported on ACNTs ($CeO_2$/ACNTs) can be prepared. The relevant chemical reactions can be expressed as follows:

$$CeCl_3 + NaOH + ACNTs \rightarrow NaCl + Ce(OH)_3/ACNTs \tag{1}$$

$$Ce(OH)_3/ACNTs \rightarrow Ce_2O_3/ACNTs + H_2O \tag{2}$$

$$Ce_2O_3/ACNTs + O_2 \rightarrow CeO_2/ACNTs \tag{3}$$

The TEM image of $CeO_2$/ACNTs is shown in Fig. 1b. It can be seen that ceria particles are homogeneously spread on the surface of ACNTs. The particle size is about 6 nm.

The Cr(VI) solution used in the batch sorption experiments was prepared by dissolving potassium dichromate ($K_2Cr_2O_7$) in deionized water. The adsorption experiments were carried out in glass tubes at room temperature (25 °C) by putting 0.1 g $CeO_2$/ACNTs in 100 ml $K_2Cr_2O_7$ solution. The effect of different pH values on Cr(VI) adsorption was studied. The pH values were adjusted with 0.1 M $HNO_3$ or 0.1 M NaOH solutions and all the pH measurements were carried out using an Elico-Digital pH meter (Model CL-51). The glass tubes were mounted on a shaker (HZQ-C) and shaken for 24 h. The suspension was filtered through 0.45 μm membrane filter. The concentration of Cr(VI) ions in solution was determined colorimetrically with the diphenylcarbazide method. The amount of Cr(VI) adsorption on the $CeO_2$/ACNTs was determined as the difference between the initial concentration and the equilibrium concentration.

## 3. Results and discussion

### 3.1. *Effect of pH*

pH is the most important parameter controlling the metal ion adsorption process. The effects of pH for Cr(VI) removal by $CeO_2$/ACNTs is shown in Fig. 2 (the initial concentration of Cr ion $C_i = 10.0\ mg\ l^{-1}$). It was apparent that Cr(VI) was strongly adsorbed at pH 3.0–7.4 and declined very sharply at pH < 3.0 and pH > 7.4.

Weng et al. (1997) found that the distribution of the Cr(VI) species in solution depends on pH: at pH value under 3.0, the dichromate ($Cr_2O_7^{2-}$) and acid chromate ($HCrO_4^-$) ion species coexist in solution. Since there are many functional groups, such as –OH and –COOH on the surface of the ACNTs after oxidation with mixed

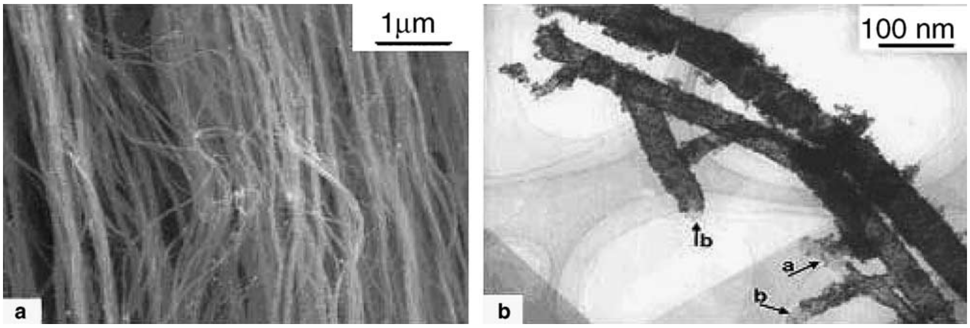

Fig. 1. (a) SEM images of ACNTs. (b) TEM image of $CeO_2$/ACNTs.