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
Al₂O₃. Here we used aligned carbon nanotubes (ACNTs) as supports to deposit CeO₂ and found that CeO₂/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 CeCl₃ (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 (CeO₂/ACNTs) can be prepared. The relevant chemical reactions can be expressed as follows:

\[ \text{CeCl}_3 + \text{NaOH} + \text{ACNTs} \rightarrow \text{NaCl} + \text{Ce(OH)}_3/\text{ACNTs} \]  
(1)

\[ \text{Ce(OH)}_3/\text{ACNTs} \rightarrow \text{Ce}_2\text{O}_3/\text{ACNTs} + \text{H}_2\text{O} \]  
(2)

\[ \text{Ce}_2\text{O}_3/\text{ACNTs} + \text{O}_2 \rightarrow \text{CeO}_2/\text{ACNTs} \]  
(3)

The TEM image of CeO₂/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 (K₂Cr₂O₇) in deionized water. The adsorption experiments were carried out in glass tubes at room temperature (25°C) by putting 0.1 g CeO₂/ACNTs in 100 ml K₂Cr₂O₇ solution. The effect of different pH values on Cr(VI) adsorption was studied. The pH values were adjusted with 0.1 M HNO₃ 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 CeO₂/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 CeO₂/ACNTs is shown in Fig. 2 (the initial concentration of Cr ion \( C_i = 10.0 \text{ mg l}^{-1} \)). 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 (\( \text{Cr}_2\text{O}_7^{2-} \)) and acid chromate (\( \text{HCrO}_4^- \)) 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
solution of nitric acid and sulfuric acid, it is supposed that CeO$_2$/ACNTs are the carbonaceous material as C$_x$OH. In the presence of a reducing substrate (C$_x$OH), Cr(VI) species are quickly reduced into Cr(III) ions as shown in Eqs. (4) and (5):

\[
3C_xOH + Cr_2O_7^{2-} + 4H^+ \rightarrow 3C_xO + HCrO_4^- + Cr^{3+} + 3H_2O \quad (4)
\]

\[
3C_xOH + HCrO_4^- + 4H^+ \rightarrow 3C_xO + Cr^{3+} + 4H_2O \quad (5)
\]

where C$_x$ = carbon. Cr(III) ions are not sorbed or poorly sorbed at these low pH values. So at pH < 3.0 the adsorption capacity is very low. Since the concentration of H$^+$ decreases at pH > 3.0, the chemical reaction (4) and (5) will not go on any more.

The pH value at which the Zeta potential equals zero is called the isoelectric point (IEP) and it is used to assess the absorbent surface charge qualitatively. The IEP of the CeO$_2$/ACNTs is 7.4 (Malvern zetameter, model zetasizer 2000). Many researchers (Wasay et al., 1996b; Tokunaga et al., 1997) have found that the adsorption of anions is the reaction between anions and the hydrous oxides of metal oxides (–M–OH) on the adsorbent surface. The hydroxylation of cerium oxides supported on ACNTs can form –Ce–OH on the surface. At pH 3.0–7.4, the main oxyanions of Cr(VI) are CrO$_4^{2-}$ and HCrO$_4^-$ ions (Weng et al., 1997) and the surface charge of CeO$_2$/ACNTs is positive, consequently, coulombic attraction can readily take place due to the interaction between Cr(VI) ions and adsorbent, and the possible ion exchange mechanisms for Cr(VI) removal can be written as follows:

\[
-Ce-OH + CrO_4^{2-} \rightarrow Ce-CrO_4^+ + OH^- \quad (6)
\]

\[
-Ce-OH + HCrO_4^- \rightarrow Ce-HCrO_4 + OH^- \quad (7)
\]

The Cr(VI) adsorption capacity of CeO$_2$/ACNTs will decrease at pH $\geq$ IEP due to neutrally or negatively charged surface of the adsorbent. In addition, at pH > 8.0 large numbers of OH$^-$ in aqueous solution will compete with Cr(VI) for the active sites.

### 3.2. Adsorption isotherms

The adsorption isotherms of Cr(VI) adsorption by CeO$_2$/ACNTs 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.

Parameter values for the Langmuir and Freundlich isotherm are listed in Table 1.

![Fig. 3. Adsorption isotherms of CeO$_2$/ACNTs as a function of pH values (25°C).](image)

#### Table 1

<table>
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<tr>
<th>pH</th>
<th>q$_m$</th>
<th>K$_L$</th>
<th>r$^2$</th>
<th>q$_m$</th>
<th>K$_F$</th>
<th>r$^2$</th>
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<td>0.4900</td>
<td>0.9958</td>
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<td>0.3181</td>
<td>0.9911</td>
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</tr>
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<td>0.9893</td>
<td>1.75</td>
<td>6.2115</td>
<td>0.9497</td>
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The experimental results based on the adsorption isotherms (Fig. 3) show that the best Cr(VI) adsorption occurs at pH 3.0–7.0. This is supported on the shape of the curve in Fig. 2. It can be seen from Fig. 3 that the mass of Cr(VI) adsorption for CeO$_2$/ACNTs at pH 7.0 reaches 30.3 mg g$^{-1}$ at equilibrium concentration of 31.4 mg l$^{-1}$. The Cr(VI) adsorption of CeO$_2$/ACNTs decreases at pH value of 9.0 and 11.0, which is 19.1 mg g$^{-1}$ and 15.6 mg g$^{-1}$, respectively. The wide range of pH values makes CeO$_2$/ACNTs good materials for Cr(VI) removal.

3.3. Comparison with other adsorbents

Cr(VI) adsorption isotherms of CeO$_2$/ACNTs were compared with ball-milled ACNTs, activated carbon EA-200 (Fujian Jianou ZhiXing Activated Carbon Co., Ltd., China) and γ-Al$_2$O$_3$.

It is can be seen from Fig. 4 that the adsorption capacity for CeO$_2$/ACNTs (28.3 mg g$^{-1}$) is about 1.5, 2.0 and 1.8 times higher than that of the activated carbon, Al$_2$O$_3$ and the ball-milled ACNTs (11.3, 9.3 and 10.2 mg g$^{-1}$), respectively, at equilibrium Cr(VI) concentration of 33.0 mg l$^{-1}$.

3.4. Mechanism of Cr(VI) adsorption by CeO$_2$/ACNTs

The most important factor in the excellent Cr(VI) adsorption capacity of CeO$_2$/ACNTs is the specific affinity between hydrous oxides of rare earth element Ce and Cr(VI) anions as shown in Eqs. (6) and (7). The small size of CeO$_2$ particles and their uniform distribution on the surface of ACNTs should contribute to the high Cr(VI) adsorption.

It is well known that the ACNTs prepared by CVD have many defects. These defects can offer active sites for Cr(VI) adsorption on the outer surfaces of ACNTs. The inner cavities and the opened ends (as shown by arrows a and b in Fig. 1b) composed by inter-aligned nanotube space may also contribute to the effective adsorption of Cr(VI). The ball-mill process will shorten ACNTs and increase the surface area of ACNTs. This is supported on the curve of the ball-milled ACNTs in Fig. 4. On the other hand, oxidation treatment by oxidized acid can cause an increase in ion-exchange capacity of ACNTs (Li et al., 2001).

4. Conclusion

Nanoparticles CeO$_2$ supported on ACNTs can be prepared by chemical reaction of CeCl$_3$ and NaOH in ACNTs solution and subsequent heat treatment. Adsorption isotherms for Cr(VI) adsorption onto CeO$_2$/ACNTs from drinking water have been studied at different pH values of the solution and found that CeO$_2$/ACNTs exhibited high Cr(VI) adsorption efficiency from water in a broad range of pH values between 3.0 and 7.4. The adsorption capacity of the CeO$_2$/ACNTs is 1.5 times higher than that of the activated carbon, 2.0 times higher than that of Al$_2$O$_3$ and 1.8 times higher than that of ball-milled ACNTs. The high adsorption capacity, the wide range of pH values make CeO$_2$/ACNTs a good candidate material for Cr(VI) removal, especially from drinking water.

References


