Short Communication

Chromium adsorption by aligned carbon nanotubes supported ceria nanoparticles

Ze-Chao Di ^{a,*}, Jun Ding ^a, Xian-Jia Peng ^b, Yan-Hui Li ^a,
Zhao-Kun Luan ^b, Ji Liang ^a^a Department of Mechanical Engineering, Tsinghua University, Beijing 100084, China^b State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

Received 21 April 2004; received in revised form 21 June 2004; accepted 24 June 2004

Abstract

Ceria nanoparticles supported on aligned carbon nanotubes (CeO₂/ACNTs), a novel adsorbent for Cr(VI) from drinking water, were prepared by chemical reaction of CeCl₃ with NaOH in aligned carbon nanotube solution and subsequent heat treatment. The best Cr(VI) adsorption effect of CeO₂/ACNTs occurs at a pH range of 3.0–7.4. The largest adsorption capacity of CeO₂/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 CeO₂/ACNTs have great potential applications in environmental protection. © 2005 Elsevier Ltd. All rights reserved.

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 adsorbents 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 adsorbent for dioxin removal. Our previous work (Li et al., 2002) suggested that carbon nanotubes show high efficiency for Pb²⁺ 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

* Corresponding author. Tel./fax: +86 10 62782413.

E-mail address: dizechao00@mails.tsinghua.edu.cn (Z.-C. Di).

Al_2O_3 . Here we used aligned carbon nanotubes (ACNTs) as supports to deposit CeO_2 and found that $\text{CeO}_2/\text{ACNTs}$ 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 $200\ \mu\text{m}$ 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 $140\ ^\circ\text{C}$ for 1 h to introduce functional groups, such as hydroxyl ($-\text{OH}$) and carboxyl ($-\text{COOH}$) 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 ($0.035\ \text{g ml}^{-1}$) 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 $450\ ^\circ\text{C}$ for 20 min. The nanosized ceria particles supported on ACNTs ($\text{CeO}_2/\text{ACNTs}$) can be prepared. The relevant chemical reactions can be expressed as follows:

The TEM image of $\text{CeO}_2/\text{ACNTs}$ 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 ($\text{K}_2\text{Cr}_2\text{O}_7$) in deionized water. The adsorption experiments were carried out in glass tubes at room temperature ($25\ ^\circ\text{C}$) by putting 0.1 g $\text{CeO}_2/\text{ACNTs}$ in 100 ml $\text{K}_2\text{Cr}_2\text{O}_7$ 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 $0.45\ \mu\text{m}$ 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 $\text{CeO}_2/\text{ACNTs}$ 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 $\text{CeO}_2/\text{ACNTs}$ 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 (HCrO_4^-) ion species coexist in solution. Since there are many functional groups, such as $-\text{OH}$ and $-\text{COOH}$ on the surface of the ACNTs after oxidation with mixed

Fig. 1. (a) SEM images of ACNTs. (b) TEM image of $\text{CeO}_2/\text{ACNTs}$.

Fig. 2. Adsorption efficiency for Cr(VI) of CeO₂/ACNTs (*R*%) as a function of pH values (*C*_i = 10.0 mg l⁻¹ and 25 °C).

solution of nitric acid and sulfuric acid, it is supposed that CeO₂/ACNTs are the carbonaceous material as C_xOH. In the presence of a reducing substrate (C_xOH), Cr(VI) species are quickly reduced into Cr(III) ions as shown in Eqs. (4) and (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 adsorbent surface charge qualitatively. The IEP of the CeO₂/ACNTs is 7.4 (Malvern zetameter, model zeta-sizer 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 CrO₄²⁻ and

HCrO₄⁻ ions (Weng et al., 1997) and the surface charge of CeO₂/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:

The Cr(VI) adsorption capacity of CeO₂/ACNTs will decrease at pH ≥ FEP 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 CeO₂/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 CeO₂/ACNTs as a function of pH values (25 °C).

Table 1

Langmuir and Freundlich isotherm parameters for Cr(VI) adsorption by CeO₂/ACNTs

pH	Langmuir			Freundlich		
	<i>q_m</i>	<i>K_L</i>	<i>r</i> ²	<i>n</i>	<i>K_F</i>	<i>r</i> ²
3.0	26.81	0.7064	0.9264	4.01	12.5021	0.9685
5.0	28.49	0.5783	0.9590	4.00	12.6493	0.9745
7.0	31.55	0.490	0.9958	4.16	13.9684	0.9488
9.0	26.04	0.3181	0.9911	2.80	8.0149	0.9697
11.0	23.26	0.2679	0.9893	1.75	6.2115	0.9497

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 CeO₂/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 CeO₂/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 CeO₂/ACNTs good materials for Cr(VI) removal.

3.3. Comparison with other adsorbents

Cr(VI) adsorption isotherms of CeO₂/ACNTs were compared with ball-milled ACNTs, activated carbon EA-200 (Fujian Jianou ZhiXing Activated Carbon Co., Ltd., China) and γ -Al₂O₃.

It can be seen from Fig. 4 that the adsorption capacity for CeO₂/ACNTs (28.3 mg g⁻¹) is about 1.5, 2.0 and 1.8 times higher than that of the activated carbon, Al₂O₃ 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 CeO₂/ACNTs

The most important factor in the excellent Cr(VI) adsorption capacity of CeO₂/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 CeO₂ particles and their uniform distribution on the surface of ACNTs should contribute to the high Cr(VI) adsorption.

Fig. 4. Adsorption isotherm of Cr(VI) on CeO₂/ACNTs compared with activated carbon, Al₂O₃ and ball-milled ACNTs (at pH = 5.0 and 25 °C).

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 CeO₂ supported on ACNTs can be prepared by chemical reaction of CeCl₃ and NaOH in ACNTs solution and subsequent heat treatment. Adsorption isotherms for Cr(VI) adsorption onto CeO₂/ACNTs from drinking water have been studied at different pH values of the solution and found that CeO₂/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 CeO₂/ACNTs is 1.5 times higher than that of the activated carbon, 2.0 times higher than that of Al₂O₃ and 1.8 times higher than that of ball-milled ACNTs. The high adsorption capacity, the wide range of pH values make CeO₂/ACNTs a good candidate material for Cr(VI) removal, especially from drinking water.

References

- Ajayan, P.M., Stephan, O., Colliex, C., Trauth, D., 1994. Aligned carbon nanotube arrays formed by cutting a polymer resin-nanotube composite. *Science* 65, 1212–1214.
- Alves, M.M., Ceca, C.G.G., de Carvalho, R.G., Castanheira, J.M., Periera, M.C.S., Vasconcelos, L.A.T., 1993. Chromium removal in tannery wastewaters polishing by *Pinus syvestris* bark. *Wat. Res.* 27, 1333–1338.
- Cao, A., Zhu, H., Zhang, X., Li, X., Ruan, D., Xu, C., Wei, B., Liang, J., 2001. Hydrogen storage of dense-aligned carbon nanotubes. *Chem. Phys. Lett.* 342, 510–514.
- Dillon, A.C., Jones, K.M., Bekkedahl, T.A., Kiang, C.H., Bethune, D.S., Heben, D.S., 1997. Storage of hydrogen in single-walled carbon nanotubes. *Nature* 386, 377–379.
- Iijima, S., 1991. Helical microtubules of graphitic carbon. *Nature* 354, 56–58.
- Jia, Z., Wang, Z., Liang, J., Wei, B., Wu, D., 1999. Production of short multi-walled carbon nanotubes. *Carbon* 37, 903–906.
- Li, Y.H., Wang, S., Cao, A., Zhao, D., Zhang, X., Xu, C., Luan, Z., Dianbo, R., Liang, J., Wu, D., Wei, B., 2001. Adsorption of fluoride from water by amorphous alumina supported on carbon nanotubes. *Chem. Phys. Lett.* 350, 412–416.

- Li, Y.H., Wang, S., Wei, J., Zhang, X., Xu, C., Luan, Z., Wu, D., Wei, B., 2002. Lead adsorption on carbon nanotubes. *Chem. Phys. Lett.* 357, 263–266.
- Long, R.Q., Yang, R.T., 2001. Carbon nanotubes as superior sorbent for dioxin removal. *J. Am. Chem. Soc.* 123, 2058–2059.
- Planeix, J.M., Coustel, N., Coq, B., Brotons, V., Kumbhar, P.S., Dutarte, R., Geneste, P., Bernier, P., Ajayan, P.M., 1994. Application of carbon nanotubes as supports in heterogeneous catalysis. *J. Am. Chem. Soc.* 116, 7935–7936.
- Selvi, K., Patabhi, S., Kadirvelu, K., 2001. Removal of Cr(VI) from aqueous solution by adsorption onto activated carbon. *Bioresour. Technol.* 80, 87–89.
- Tokunaga, S., Wasay, S.A., Park, S.W., 1997. Removal of arsenic(V) ion from aqueous solutions by lanthanum compounds. *Wat. Sci. Technol.* 35, 71–78.
- Wang, Q.H., Setlur, A.A., Lauerhaas, J.M., Dai, J.Y., Seelig, E.W., Chang, R.P.H., 1998. A nanotube-based field-emission flat panel display. *Appl. Phys. Lett.* 72, 2912–2913.
- Wasay, S.A., Haron, M.J., Tokunaga, S., 1996a. Adsorption of fluoride, phosphate, and arsenate ions on lanthanum-impregnated silica gel. *Wat. Environ. Res.* 68, 295–300.
- Wasay, S.A., Haron, J., Uchiumi, A., Tokunaga, S., 1996b. Removal of arsenate and arsenite ions from aqueous solution by basic yttrium carbonate. *Wat. Res.* 30, 1143–1148.
- Weng, C.H., Wang, J.H., Huang, C.P., 1997. Adsorption of Cr(VI) onto TiO₂ from dilute aqueous solutions. *Wat. Sci. Technol.* 35, 55–62.
- Yabe, M.J.S., Oliveira, E., 2003. Heavy metals removal in industrial effluents by sequential adsorbent treatment. *Adv. Environ. Res.* 7, 263–272.