

# Ceria nanoparticles supported on carbon nanotubes for the removal of arsenate from water

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## Abstract

A novel adsorbent, ceria supported on carbon nanotubes (CeO<sub>2</sub>-CNTs), was developed for the removal of arsenate from water. The experiments show that CeO<sub>2</sub>-CNTs is an effective adsorbent for arsenate, and the adsorption is pH-dependent. Ca<sup>2+</sup> and Mg<sup>2+</sup> significantly enhanced its adsorption capacity, which suggests that it is a promising adsorbent for drinking water purification. Under natural pH conditions, an increase from 0 to 10 mg/L in the concentration of Ca<sup>2+</sup> and Mg<sup>2+</sup> results in an increase from 10 to 81.9 and 78.8 mg/g in the amount of As(V) adsorbed, respectively. The loaded adsorbent can be efficiently regenerated by diluted NaOH, and a regeneration efficiency of 94% was achieved using 0.1 mol/L NaOH. The adsorption mechanism was also suggested.

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## 1. Introduction

Since Iijima's observations in 1991 [1], carbon nanotubes (CNTs) have been the subject of an increasing number of experimental and theoretical studies. CNTs have unique mechanical, electrical, optical, and thermal properties and can be used to prepare novel materials, such as hydrogen storage materials [2], superconductors [3], reinforced materials [4], etc. Their cylindrically layered and hollow tubule nanostructures with high thermal and chemical stabilities make them possible to function as supports for preparing nanosized metal and metal oxide particle catalysts. Many kinds of metals have been successfully supported on CNTs [5–7]. Because of their large specific area, CNTs can also be used as supports for adsorption materials. In this paper, ceria supported on CNTs was prepared as a novel adsorbent for the removal of arsenate in water purification.

Arsenic pollution of water occurs due to various reasons, such as natural leaching of rocks containing arsenic, mining, processing of mineral deposits and discharge of industrial pollutants [8]. Although arsenic is needed as a micronutrient for human body, it is carcinogenic when consumed in larger quantities over a period. Hence, it is of great importance to remove arsenic before water can be used for drinking in arsenic-contaminated areas. Adsorption is one of the major methods employed for the removal of arsenic from water. Many kinds of adsorbents, such as carbon, rare earth oxides, lanthanum and yttrium impregnated alumina, amorphous iron hydroxide, polymers loaded with monoclinic hydrous zirconium oxide, ion exchange fiber, and lanthanum compounds, have been developed for the removal of arsenic from water [8–13]. Ceria has been reported to have good adsorption capacity for the removal of some anions and high resistance against attacks by acid [14]. Otherwise, cerium is a rather cost-effective element with rather large reserves among rare earth elements. Here, ceria was supported on carbon nanotubes as nanoparticles, and the resulting

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material was reported to have good arsenate adsorption capacity from water in this paper.

## 2. Experimental

### 2.1. Materials

CNTs were prepared by catalytic pyrolysis of the propylene-hydrogen ( $C_3H_6/H_2=2:1$ ) mixture at  $750\text{ }^\circ\text{C}$  in a ceramic tube furnace using Ni particles as catalysts. The CNTs were then washed with deionized water and ground. The oxidized CNTs were prepared by refluxing the as-prepared CNTs with mixed solution of nitric acid and sulfuric acid at  $140\text{ }^\circ\text{C}$  to introduce oxygen groups, such as hydroxyl ( $-OH$ ) and carboxyl ( $-COOH$ ), on the surface of CNTs. These groups can preserve the suspensibility of CNTs in solution and may be beneficial to the adhesion of  $Ce(OH)_3$  particles on the wall of CNTs. The ceria supported on carbon nanotubes was prepared as follows [7]: 1 g CNTs were dispersed into 20 mL distilled water and agitated with a magnetic agitator. The  $CeCl_3$  (0.035 g/mL) solution was added into the CNTs solution drop by drop. After the mixture was agitated for 1 h, 0.5 wt.% NaOH was titrated into the mixture until the pH value reaches 9. The mixture was then dried up and heated in air at  $450\text{ }^\circ\text{C}$  for 20 min to oxidize  $Ce(OH)_3$  particles to  $CeO_2$  nanoparticles. The nanosized ceria particles supported on CNTs can be prepared. Stock solution of 1000 mg/L As(V) was prepared by dissolving appropriate quantities of analytical grade dibasic sodium arsenate in deionized water. The stock solution was further diluted to suitable concentrations.

### 2.2. Methods

Zeta potential and points of zero charge (PZC) for the adsorbent were determined by microelectrophoresis using a Malvern model Zetasizer 2000 zeta potential analyzer. The zeta potentials of the adsorbent suspensions containing 0.02% solid in 0.01 M NaCl were determined at various pH values. The PZCs were obtained by interpolating the data to zero zeta potential. The specific area of the adsorbents was measured by nitrogen adsorption/desorption at 77 K using BET method.

Batch adsorption experiments were performed in glass bottles. To each bottle, 50 mL As(V) solution of prescribed concentration and 0.025 g adsorbent were added. The pH was adjusted using 1 M HCl or 1 M NaOH. The bottles were capped with glass screws and then were shaken on a HZQ-C shaker for 24 h. After equilibrium, the solution was centrifuged and the residual concentrations of As(V) in the supernatant solution was analyzed using a Rayleigh model AF-610A atomic fluorescence spectrometer. As(V) adsorbed was calculated. Desorption experiments using NaOH and HCl were

carried out. For desorption experiments, first As(V) was adsorbed according to the same procedure described above. After adsorption, suspensions were centrifuged. The supernatant was decanted and analysed for As(V). Then 50 mL of NaOH or HCl solution (0.005–0.05 M) was added to the loaded particles. The samples were then shaken for 2 h and centrifuged. As(V) concentration in the supernatant was analyzed, and regeneration efficiency was calculated.

## 3. Results and discussion

The X-ray diffraction (XRD) pattern and transmission electron microscopy (TEM) image of ceria supported on CNTs ( $CeO_2$ -CNTs) are shown in Figs. 1 and 2. There are two peaks corresponding to the (002) and the (101) of CNTs in the XRD pattern, and it shows that the nanosized ceria particle and the CNTs possess good crystalline structures. The TEM image show that ceria particles are homogeneously spread on the surface of CNTs with a particle size of about 6 nm. The specific area of oxidized CNTs and  $CeO_2$ -CNTs are  $153\text{ m}^2/\text{g}$  and  $189\text{ m}^2/\text{g}$ , respectively. It indicates that the deposition of nanosized particles of ceria increases the surface area.

The zeta potentials of  $CeO_2$ -CNT at various pH were shown in Fig. 3. For comparison, Zeta potentials of oxidized CNTs were also included. As can be seen from Fig. 3, Zeta potentials of both  $CeO_2$ -CNTs and oxidized CNTs decrease with the increase in pH.  $CeO_2$ -CNTs have positive Zeta potentials when  $pH < 5.5$ , which indicates that they are positively charged, and negative Zeta potentials when  $pH > 6.4$ , which indicates that they are negatively charged. The PZC of  $CeO_2$ -CNTs occurs at pH 5.5–6.4. Zeta potentials of oxidized CNTs remain negative in the pH range  $\sim 3\text{--}10$ , which indicates that they are negatively charged. As(V) exists as anions in aqueous solution. The electrostatic interaction between oxidized CNTs and As(V) anions is repulsion, which decreases the adsorption. During the pH range of  $\sim 3\text{--}10$ ,  $CeO_2$ -CNTs have much higher Zeta potentials than oxidized CNTs. The increased Zeta

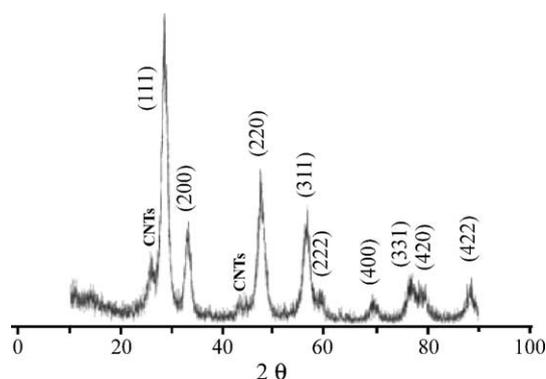
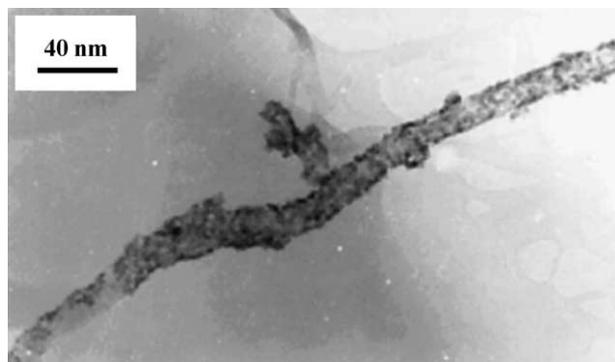
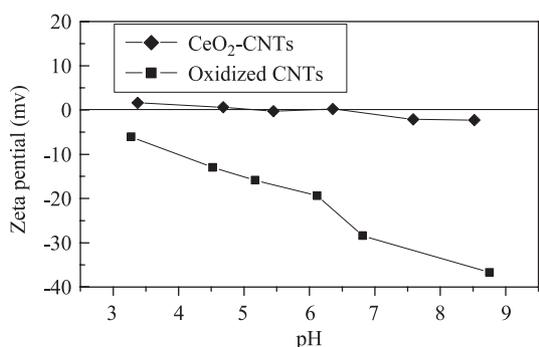
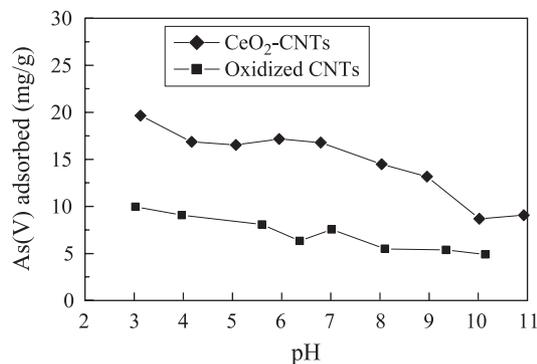


Fig. 1. XRD pattern of  $CeO_2$ -CNTs.

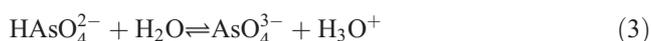
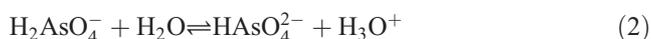
Fig. 2. TEM image of CeO<sub>2</sub>-CNTs.

potential resulting from the deposition of ceria on oxidized CNTs can be expected to decrease the electrostatic repulsion. Moreover, at pH < PZC, the electrostatic interaction between positively charged CeO<sub>2</sub>-CNTs and As(V) anions is attraction. The electrostatic attraction can facilitate the adsorption.

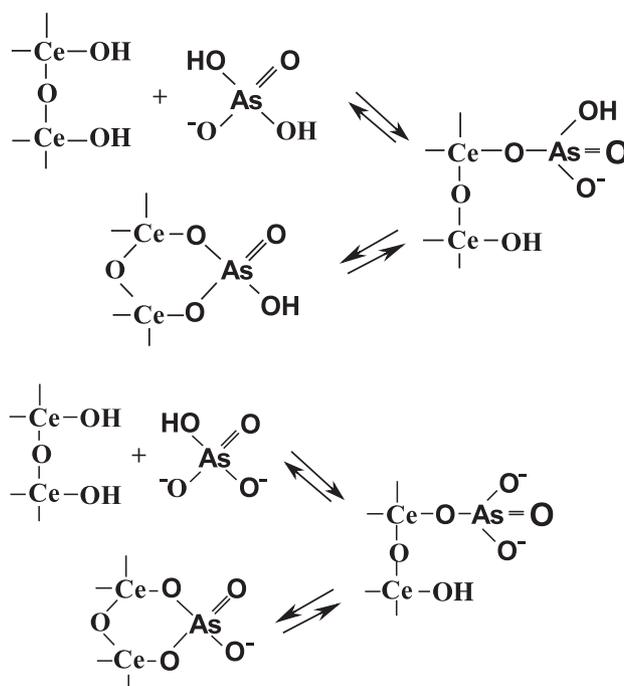
The effect of pH on the adsorption of As(V) to CeO<sub>2</sub>-CNTs is shown in Fig. 4. For comparison, the use of oxidized CNTs for As(V) adsorption was also included. Fig. 4 shows that the adsorption of As(V) to CeO<sub>2</sub>-CNTs is pH-dependent. CeO<sub>2</sub>-CNTs have higher adsorption capacity than oxidized CNTs. Adsorption of As(V) to CeO<sub>2</sub>-CNTs decreases with the increase in pH. An increase in pH from 3.1 to 10.0 results in a decrease from 19.7 to 8.7 mg/g in the amount of As(V) adsorbed. The dependence of adsorption on pH values is due to the dependence of the surface charge of CeO<sub>2</sub>-CNTs on pH values, which has been shown by Zeta potential measurements. At pH < PZC, the surface charge of CeO<sub>2</sub>-CNTs is positive, and coulombic attraction can readily take place between the positively charged adsorbent particles and negatively charged As(V) ions. Adsorption of As(V) decreases at pH > PZC due to negatively charged adsorbent surface. Many researchers [9,13,15–17] have found that the adsorption of anions is the reaction between anions and the –MOH or –MOH<sub>2</sub><sup>+</sup> on the adsorbent surface. The hydroxylation of cerium oxides supported on CNTs can form –Ce–OH and –Ce–OH<sub>2</sub><sup>+</sup> on the

Fig. 3. Zeta potentials of CeO<sub>2</sub>-CNTs and oxidized CNTs.Fig. 4. The effect of pH on the adsorption ( $C_0=20$  mg/L,  $t=24$  h,  $m=0.025$  g).

surface. In the solution, the following chemical equilibriums exist:



In the pH range 3–7, H<sub>2</sub>AsO<sub>4</sub><sup>–</sup> is the predominant species, and in the pH range 7–10, HASO<sub>4</sub><sup>2–</sup> is the predominant species. A mechanism for the adsorption of As(V) on goethite (α-FeOOH) in a two-step process has been proposed by Grossl et al. [18]. Based on this model, the mechanism for the adsorption of As(V) to CeO<sub>2</sub>-CNTs can be explained as follows:

Fig. 5 shows adsorption isotherms of CeO<sub>2</sub>-CNTs. The Freundlich model was employed for adsorption of CeO<sub>2</sub>-

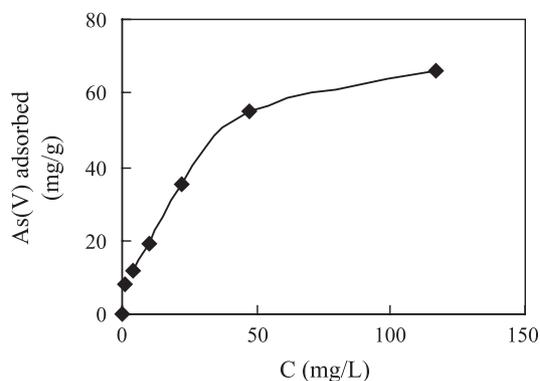


Fig. 5. Adsorption isotherms of CeO<sub>2</sub>-CNTs ( $m=0.025$  g,  $t=24$  h, pH 3.1).

CNTs. Freundlich adsorption isotherm represents the relationship between the amount of adsorbate adsorbed by per unit mass of adsorbent ( $q_e$ ) and the concentration of adsorbate at equilibrium ( $C_e$ ):

$$q_e = KC_e^{\frac{1}{n}} \quad (4)$$

or:

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad (5)$$

$K$  and  $n$  are constants representing the adsorption capacity and intensity of the adsorption, respectively. The experimental data fit the Freundlich adsorption isotherm well with a correlation coefficient of 0.964.

Ca<sup>2+</sup> and Mg<sup>2+</sup> always exist in natural water. In order to assess the potential application of CeO<sub>2</sub>-CNTs for the removal of As(V) from natural water, adsorption capacity was evaluated as a function of Ca<sup>2+</sup> and Mg<sup>2+</sup> concentration. The adsorbent is aimed to be used in drinking water purification, therefore adsorption studies were carried out without pH adjustment. The results are shown in Fig. 6. It can be seen that Ca<sup>2+</sup> and Mg<sup>2+</sup> significantly enhance the adsorption capacity of CeO<sub>2</sub>-CNTs. An increase from 0 to 10 mg/L in the concentration of Ca<sup>2+</sup> and Mg<sup>2+</sup> results in an increase from 10 to 81.9 and 78.8 mg/g in the amount of As(V) adsorbed, respectively. When the concentrations of Ca<sup>2+</sup> and Mg<sup>2+</sup> exceed 10 mg/L, the removal remains

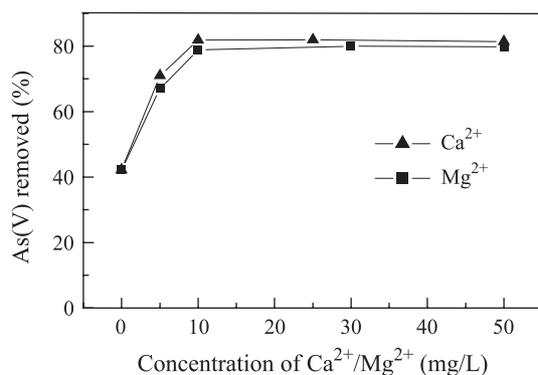


Fig. 6. The effect of Ca<sup>2+</sup> and Mg<sup>2+</sup> on adsorption ( $C_0=20$  mg/L,  $m=0.025$  g,  $t=24$  h).

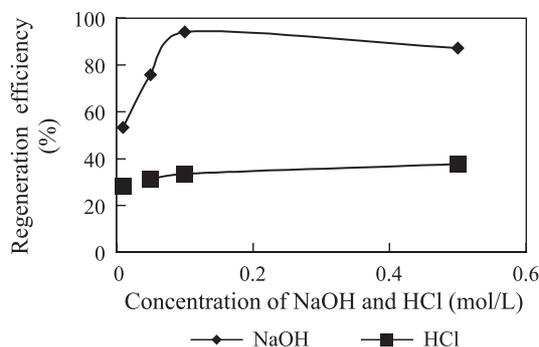
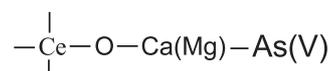


Fig. 7. The effect of NaOH/HCl concentration on desorption.

constant, and 80% As(V) removal was observed. The increased adsorption capacity with Ca<sup>2+</sup> and Mg<sup>2+</sup> existence can be explained by the ternary surface complex reaction [19,20]. The cations exchange with the surface groups first and then As(V) anions is combined to the liquid–solid interface, and the following surface complex forms:



The increased adsorption capacity with Ca<sup>2+</sup> and Mg<sup>2+</sup> existence suggests that CeO<sub>2</sub>-CNTs is a promising adsorbent for the removal of As from drinking water.

The applicability of adsorbents depends not only on the adsorption capacity, but also on the desorption property. NaOH and HCl were selected as regeneration agents in this work. In the desorption experiments, in order to show the desorption property of CeO<sub>2</sub>-CNTs as adsorbent for purification of natural water, first, As(V) was adsorbed from a 20 mg/L solution containing 10 mg/L Ca<sup>2+</sup>. The effect of the concentration of regeneration agents on desorption efficiency is plotted in Fig. 7. The low desorption was observed using HCl, and the regeneration efficiency is below 40%. It can be seen that diluted NaOH is efficient for the regeneration. The regeneration efficiency reaches 94% when the concentration of NaOH reaches 0.1 mol/L, which suggests that As(V)-loaded CeO<sub>2</sub>-CNTs can be efficiently regenerated by NaOH solution.

#### 4. Conclusion

A novel adsorbent, ceria supported on CNTs, has been developed, and batch adsorption experiments were carried out to evaluate its adsorption capacity for As(V) from water. The experiments show that CeO<sub>2</sub>-CNTs have much higher zeta potentials than oxidized CNTs and can be expected to reduce the repulsion between its particles and negatively charged substances and enhance the removal of these substances from water. CeO<sub>2</sub>-CNTs adsorption is pH-dependent due to the dependence of the surface charge of

CeO<sub>2</sub>-CNTs on pH values. Ca<sup>2+</sup> and Mg<sup>2+</sup> significantly enhance its adsorption capacity due to the ternary surface complex reaction among solid surface, cations, and As(V) anions. Under natural pH conditions, an increase from 0 to 10 mg/L in the concentration of Ca<sup>2+</sup> and Mg<sup>2+</sup> results in an increase from 10 to 81.9 and 78.8 mg/g in the amount of As(V) adsorbed, respectively, which suggests that CeO<sub>2</sub>-CNTs are a potential adsorbent for the removal of As from drinking water. The As(V)-loaded adsorbent can be efficiently regenerated by diluted NaOH, and a high regeneration efficiency of 94% was achieved using 0.1 mol/L NaOH.

## References

- [1] S. Iijima, Nature 354 (1991) 56.
- [2] S.M. Lee, Y.H. Lee, Appl. Phys. Lett. 76 (2000) 2877.
- [3] K. Fossheiheim, E.D. Tuset, T.W. Ebbesen, M.M.J. Treacy, J. Schwartz, Physica C 248 (1995) 195.
- [4] T. Kuzumaki, K. Miyazawa, H. Ichinose, K. Ito, J. Mater. Res. 13 (1998) 2445.
- [5] J.M. Planeix, N. Coustel, B. Coq, et al., J. Chem. Soc. 116 (1994) 7935.
- [6] G. Che, B.B. Lakshmi, E.R. Fisher, et al., Nature 393 (1998) 346.
- [7] Y. Li, J. Ding, J. Chen, et al., Mater. Res. Bull. 37 (2002) 313.
- [8] A.M. Raichur, V. Panvekar, Sep. Sci. Technol. 37 (2002) 1095.
- [9] S.A. Wasay, S. Tokunaga, S.W. Park, Sep. Sci. Technol. 31 (1996) 1501.
- [10] M.L. Pierce, C.B. Moore, Water Res. 16 (1982) 1247.
- [11] T.M. Suzuki, M.L. Tanco, D.A.P. Tanaka, et al., Sep. Sci. Technol. 36 (2001) 103.
- [12] R. Liu, J. Guo, H. Tang, J. Colloid Interface Sci 248 (2002) 268.
- [13] S. Tokunaga, S.A. Wasay, S.W. Park, Water Sci. Technol. 35 (7) (1997) 71.
- [14] S. Tokunaga, M.J. Harson, S.A. Wasay, Int. J. Environ. Stud. 48 (1995) 17.
- [15] S.A. Wasay, M.J. Haron, A. Uchiumi, S. Tokunaga, Water Res. 30 (1996) 1143.
- [16] S.A. Wasay, M.J. Haron, S. Tokunaga, Water Environ. Res. 68 (3) (1996) 295.
- [17] C. Namasivayam, S. Senthikumar, Ind. Eng. Chem. Res. 37 (1998) 4816.
- [18] P.R. Grossl, M. Eick, D.L. Sparks, S. Goldberg, C.C. Ainsworth, Environ. Sci. Technol. 31 (1997) 321.
- [19] Z. Zhang, L. Liu, H. Zhao, et al., J. Colloid Interface Sci. 182 (1996) 158.
- [20] W. Zhao, Z. Zhang, J. Ocean Univ. Qingdao 27 (2) (1997) 233, (In Chinese).