



Mutual promotion mechanism for adsorption of coexisting Cr(III) and Cr(VI) onto titanate nanotubes



Wen Liu^{a,b}, Hao Chen^a, Alistair G.L. Borthwick^c, Yunfei Han^b, Jinren Ni^{a,b,*}

^aShenzhen Key Laboratory for Heavy Metal Pollution Control and Reutilization, School of Environment and Energy, Peking University Shenzhen Graduate School, Shenzhen 518055, China

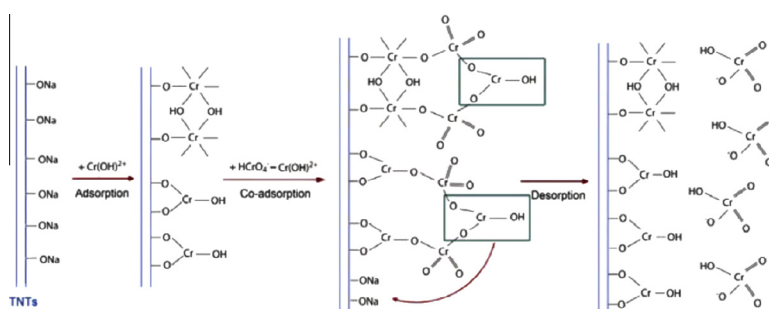
^bThe Key Laboratory of Water and Sediment Sciences, Ministry of Education, Department of Environmental Engineering, Peking University, Beijing 100871, China

^cDepartment of Civil & Environmental Engineering, University College Cork, Cork, Ireland

HIGHLIGHTS

- TNTs showed large adsorption capacity for Cr(III) with mechanism of ion-exchange.
- Mutual promotion on adsorption of Cr(III) and Cr(VI) was found in wide pH ranges.
- Formation of Cr(III)—O—Cr(VI) linkages resulted in double-layer adsorption.
- Cr(III) rearranged from second layer to TNTs at unsaturated adsorption.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 8 June 2013

Received in revised form 19 July 2013

Accepted 22 July 2013

Available online 3 August 2013

Keywords:

Titanate nanotubes
Double-layer adsorption
Hexavalent chromium
Trivalent chromium
Rearrangement

ABSTRACT

Multilayered titanate nanotubes (TNTs) were shown to provide excellent adsorption of Cr(III), with a maximum adsorption capacity of 88.99 mg g⁻¹. Adsorption of Cr(III) and Cr(VI) was mutually promoted when the two ions coexisted at wider pH ranges of 3–6. Compared to single systems, the adsorption capacity of Cr(III) increased from 56.3 to 82.1 mg g⁻¹, whereas the Cr(VI) capacity increased from 0 to 9.8 mg g⁻¹ in the binary system at pH 5 with 0.6 g L⁻¹ TNTs. Cr(III) adsorbed onto the TNTs mainly through ion-exchange with Na⁺ in the interlayers of TNTs, as indicated by the linear relationship between adsorption capacity of Cr(III) and the Na content of TNTs. However, double-layer adsorption occurred when Cr(III) and Cr(VI) coexisted. An ionic cluster of Cr(III) and Cr(VI) was formed initially and subsequently bridged with Cr(III) adsorbed on TNTs through Cr(III)—O—Cr(VI) linkages. X-ray photoelectron spectroscopy (XPS) and Raman analyses confirmed the ion-exchange mechanism and formation of Cr(III)—O—Cr(VI), and that the process did not change the basic [TiO₆] structure of TNTs. Moreover, rearrangement of Cr(III) from the second layer to TNTs' surface was observed when adsorption of Cr(III) was unsaturated, resulting in damage to Cr(III)—O—Cr(VI) linkages and desorption of Cr(VI).

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Chromium (Cr) is a highly toxic water contaminant that commonly occurs in industrial effluent from electroplating, tanning, mining, etc. [1,2]. Hexavalent (Cr(VI)) and trivalent (Cr(III))

chromium are the two main forms of chromium found in the aqueous environment. Cr(VI) is particularly damaging to plants and aquatic organisms, and is harmful to human beings when ingested through the respiratory tract, digestive tract, or skin [1,2]. Conventional technologies like precipitation, reverse osmosis, ion

* Corresponding author at: Shenzhen Key Laboratory for Heavy Metal Pollution Control and Reutilization, School of Environment and Energy, Peking University Shenzhen Graduate School, Shenzhen 518055, China. Tel.: +86 10 6275 1185; fax: +86 10 6275 6526.

E-mail address: nijinren@iee.pku.edu.cn (J. Ni).

exchange, adsorption, etc. are generally used to remove Cr from wastewaters [3–6]. In practice, Cr(VI) is always reduced initially to Cr(III) which is a less toxic form of chromium, and this is then subject to further treatment [7,8]. Given the complicated chemistry of chromium-containing wastewater and the incomplete reduction of Cr(VI) by conventional treatment technologies, Cr(III) and Cr(VI) always coexist in the effluent wastewater. However, few studies to date have focused on the interaction between Cr(III) and Cr(VI) in water treatment process.

Of the technologies presently available for Cr removal, adsorption appears most promising because of its high efficiency, low cost and simple operation [9,10]. In recent decades, titanate nanotubes (TNTs) have been used as heavy-metal adsorbents, owing to the nanotubes' large surface area which promotes abundant –OH sites [11,12]. Xiong et al. [13] reported that TNTs were excellent at adsorbing Pb(II) and Cd(II), with measured adsorption capacities of 520.83 mg g⁻¹ and 238.61 mg g⁻¹, respectively. Li et al. [14] obtained 99.8% removal efficiency of Cu(II) on TNTs for an initial concentration of 100 mg L⁻¹ of Cu(II) at pH 4. Niu [15] found that protonated titanate nanotubes performed well at adsorbing arsenic and arsenate. Besides, adsorption of lanthanide Eu(III) and influence of solution chemistry on adsorption of Ni(II) on TNTs were also studied [16–18]. However, although previous studies [19–22] have demonstrated that Cr(III) and Cr(VI) could be efficiently removed by TNTs or amino-functionalized TNTs, the adsorption behavior of coexisting Cr(III) and Cr(VI) on TNTs has received scant attention to date.

This paper first examines the adsorption kinetics and isotherms of Cr(III) on TNTs in single systems. Co-adsorption of Cr(III) and Cr(VI) in binary systems is then investigated considering the effects of pH, initial concentration ratio (of the two ions), and TNTs dosage. Afterwards, the co-adsorption mechanisms of Cr on TNTs, as well as the interactions between Cr(III), Cr(VI) and TNTs are explained by means of X-ray photoelectron spectroscopy (XPS), Raman spectra, Fourier transform infrared (FT-IR) spectroscopy and X-ray diffraction (XRD) analysis.

2. Materials and methods

2.1. Materials and chemicals

Stock solutions (1000 mg L⁻¹) of Cr(III) and Cr(VI) were prepared by dissolving analytical grade Cr(NO₃)₃·12H₂O and K₂Cr₂O₇ in deionized water. Degussa-TiO₂ nanoparticles (P25, 80% anatase and 20% rutile, an average particle size of 20–30 nm) were purchased for synthesis of the TNTs. All other reagents used in the experiments were of analytical grade or better.

2.2. Preparation of titanate nanotubes

Titanate nanotubes were prepared by a hydrothermal method following Chen et al. and Xiong et al. [11,13,23]. Specifically, 1.2 g TiO₂ nanoparticles and 29.04 g NaOH of guaranteed grade were mixed with 66 mL deionized water. Afterwards, the mixture was transferred into a Teflon-lined autoclave (100 mL) and then heated at 130 °C for 72 h. Finally, the precipitates were washed with deionized water until the supernatant was neutral, and TNTs were obtained after drying at 80 °C for 4 h.

2.3. Adsorption of Cr(III) onto TNTs in single systems

2.3.1. Kinetics and equilibrium experiments

Kinetics experiments were conducted for initial Cr(III) concentrations of 30, 40 and 50 mg L⁻¹. 0.12 g of TNTs were added into 200 mL of Cr(III) solutions. After the pH was adjusted to 5 using

diluted HCl and NaOH solutions, the suspension was shaken for 4 h at 25 °C and 200 rpm using a table concentrator. Samples were taken at specific intervals, and then filtered through a 0.22 μm membrane, ready for further analysis. In the equilibrium experiments, Cr(III) solutions (50 mL, pH 5) with initial concentrations varying from 0 to 120 mg L⁻¹ were mixed with 0.03 g of TNTs. After shaking for 3 h, samples were extracted and filtered.

The concentration of Cr(III) was determined by means of inductively-coupled plasma-optical emission spectrometry (ICP-OES, Prodigy, USA). The adsorption capacity of Cr(III) on TNTs is calculated by:

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where Q_e (mg g⁻¹) is the adsorption capacity of metals at equilibrium, V (L) is the total volume of solution, C_0 and C_e (mg L⁻¹) are the initial and equilibrium mass concentrations of Cr(III) respectively, and m is the mass of TNTs (g).

The removal efficiency (R) is defined as:

$$R = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (2)$$

2.3.2. Adsorption experiments using TNTs with different Na contents

About 0.4 g pre-prepared TNTs were immersed in 200 mL HNO₃ solutions whose pH ranged from 1 to 5. After stirring for 5 min, the products were washed with deionized water until the supernatant was neutral, and then dried for 4 h in an oven. 0.015 g of products were dissolved into 5 mL of 15 mol L⁻¹ HNO₃, and the Na⁺ concentration was determined by ICP-OES after dilution. In the adsorption experiments, 50 mL of 50 mg L⁻¹ Cr(III) solution were mixed with 0.03 g of TNTs of different Na⁺ contents at pH 5, and the Cr(III) concentrations of the samples were measured after shaking for 3 h.

2.4. Co-adsorption of Cr(III) and Cr(VI) onto TNTs in binary systems

Experiments on the co-adsorption of Cr(III) and Cr(VI) by TNTs in binary systems were carried out as follows: (1) Effect of pH. A mixed solution (50 mL) of Cr(III) and Cr(VI) was prepared, and the initial concentration of the two ions was 50 and 10 mg L⁻¹, respectively. After the solution pH was adjusted from 1 to 6, 0.03 g TNTs were added, and then shaken for 3 h. Control tests were conducted for individual Cr(III) of 50 mg L⁻¹ and Cr(VI) of 10 mg L⁻¹. (2) Effect of concentration ratio of Cr(III) to Cr(VI). In a mixed solution of 50 mL at pH 5, the initial concentration of Cr(VI) was fixed at 10 mg L⁻¹ and the Cr(III) concentration varied from 20 to 50 mg L⁻¹. (3) Effect of adsorbent dosage. TNTs were added, with the dosage ranging from 0.2 to 0.9 g L⁻¹, to a 50 mL mixed solution of 50 mg L⁻¹ Cr(III) and 10 mg L⁻¹ Cr(VI), after the pH was adjusted to 5.

In the binary systems, the concentration of Cr(VI) was determined using a ultraviolet spectrophotometer (UV1800, Shimadzu, Japan) with diphenylcarbohydrazide as the chromogenic agent [21]. The concentration of total Cr was measured by ICP-OES, and then the concentration of Cr(III) obtained as the difference between total Cr and Cr(VI).

2.5. Analytical and characterization methods

After adsorption of Cr(III) (initial concentration was 50 mg L⁻¹) and co-adsorption of Cr(III) and Cr(VI) (initial concentration was 50 and 10 mg L⁻¹, respectively) at pH 5 with a adsorbent dosage of 0.6 g L⁻¹, TNTs were separated and dried in air for further characterization. Specifically, the original TNTs, TNTs with Cr(III) Transmission electron microscopy (TEM) analysis was conducted using a Tecnai T20 microscope (FEI, USA) operating at 200 kV, and which

Download English Version:

<https://daneshyari.com/en/article/148138>

Download Persian Version:

<https://daneshyari.com/article/148138>

[Daneshyari.com](https://daneshyari.com)