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Research paper

Sequestration of selenate and selenite onto titanate nanotube: A combined classical batch and advanced EXAFS approach

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ABSTRACT

The sequestration of selenate (Se(VI)) and selenite (Se(IV)) onto titanate nanotubes (TNTs) via an adsorption was studied using a combination of macroscopic interaction data, zeta potential determinations and X-ray absorption fine structure (XAFS) analyses. The macroscopic interaction results showed generally increased adsorption of Se(VI)/Se(IV) onto TNTs with pH decreasing, and indicated an ionic strength-dependent adsorption of Se(VI) onto TNTs, whereas an ionic strength-(in)dependent adsorption of Se(IV) onto TNTs. Besides, we observed that both Se(VI) and Se(IV) decreased the zeta potential of TNTs upon adsorption. Nevertheless, only Se(IV) adsorption decreased the pH_{PZC} of TNTs. The X-ray absorption fine structure (XAFS) results pointed to substantial differences of the adsorption mode for Se(VI)/Se(IV) onto TNTs, with Se(VI) adsorbing as an outer-sphere surface complex, and Se(IV) coordinating as an inner-sphere surface complex. Combined, the results presented here showed that pH and ionic strength are major factors in determining the adsorption extent and model of Se(VI)/Se(IV) onto TNTs. In a word, TNTs exhibited excellent adsorption capacity to both Se(VI) and Se(IV) regardless their different adsorption mode. Hence, as the synthesis equipment is cheap and simple, TNTs can be regarded as a low-cost sequestrator for the efficient trapping of selenium in water.

1. Introduction

Disposal of industrial wastewater has increasingly becoming one of the most pressing issues over the whole world, since these effluents usually contain considerable amount of heavy metal ions including Pb(II), Ni(II), Cu(II), Zn(II), Cd(II), Eu(III), As(V)/(III), Cr(VI) and Se(VI)/(IV) (Huang et al., 2012; Sheng et al., 2016a,b,c,d, 2014a,c, 2012a,b, 2011, 2013a, 2009; Zhao et al., 2011, 2010; Yang et al., 2010, 2011; Xu et al., 2008; Hu et al., 2010). These heavy metal ions, anthropogenic origins of which includes wastewater of many industries like batteries, metal-plating, pesticides, pigments and plastics manufacturing, are highly toxic and can cause potential damage to human beings or the natural water and soil environment (Huang et al., 2012; Sheng et al., 2016a,c, 2014a,c, 2012a; Zhao et al., 2011; Yang et al., 2010). Therefore, effective treatment and remediation of heavy metal ions from wastewater are very significant for the protection of natural environment and public health.

To date, a large number of remediation approaches which included adsorption, ion exchange, evaporation, chemical reduction, surface precipitation and membrane filtration have been utilized for the effective treatment of heavy metal ions from wastewater (Huang et al., 2012; Sheng et al., 2016a,c, 2014a,c, 2012a, 2011, 2013a; Zhao et al., 2011; Yang et al., 2010). Among these approaches, it has been proved that adsorption is one of the most attractive and effective approaches (Zhao et al., 2011, 2010; Sheng et al., 2014a,c, 2012a,b, 2011, 2013a; Yang et al., 2010, 2011; Xu et al., 2008; Hu et al., 2010). In this respect, lots of potential adsorbents including layered double hydroxide, carbon-based materials, natural oxide and clay minerals have been tested to treat metal ions from wastewater (Zhao et al., 2011, 2010; Sheng et al., 2014a,c, 2012a,b, 2011, 2013a; Yang et al., 2010, 2011; Xu

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et al., 2008; Hu et al., 2010). Recently, artificial titanate nonmaterial has become more and more attractive to be applied as promising adsorbents in the removal of metal ions due to their outstanding properties. For instance, titanate nanotubes (TNTs) which can be derived from a hydrothermal approach not only possess flexible interlayer distances and high surface area, but also displays high cation exchange capacity and high density of functional hydroxyl group on the surface (Huang et al., 2012; Liu et al., 2014a,b,c 2013a,b, 2016; Sheng et al., 2014b, 2013b, 2015; Sheng and Hu, 2013; Wang et al., 2013a,b). All of these characteristics are quite important to enhance the adsorption rate and capacity of TNTs. It has been reported that a large number of metal ions could be effectively sequestered onto titanate nanomaterials (Huang et al., 2012; Liu et al., 2014a,b,c, 2013a, 2016, 2013b; Sheng et al., 2014b, 2013b, 2015; Sheng and Hu, 2013; Wang et al., 2013a,b). In our previous work, we investigated the sequestration of different metal ions with various valence state (i.e, Ni(II), Eu(III), Th(IV), U(VI)) onto TNTs as a function of water quality parameters, and found that TNTs showed good adsorption capacity to these ions (Sheng et al., 2014b, 2013b, 2015; Sheng and Hu, 2013). Ni and co-authors conducted a systematic investigations into the adsorption of Pb^{2+}, Tl^{+}, Tl^{3+}, U^{6+}, Cd^{2+}, Cu^{2+} and Cr^{3+} onto TNTs as affected by solution chemistry. Nevertheless, most of these studies were concentrated on the sorption of cations onto TNTs, little attention has been paid to the sorption of anions onto TNTs (Liu et al., 2013a, 2014c). It is well known that selenium (Se) is a toxic element if it is taken in excess and a possible carcinogen to humans. In the past decades, Se has been commonly regarded as a potential contaminant which was derived from oil refinery, coal-fire power plants, mining industries, etc. Besides, Se exits in several oxidation states (Se(VI), Se(IV), Se(0), Se(-II)) in the natural environment (Liang et al., 2013, 2014a,b, 2015; Li et al., 2014). The anionic species with higher oxidation states, i.e., selenate ($SeO_4{}^{2-}$) or selenite ($SeO_3{}^{2-}$), whose toxicity in mice as LD50 was previously reported 5.5 $mgkg^{-1}$ for selenate, and 3.5 $mg\,kg^{-1}$ for selenite (O'Brien et al., 2003), are highly soluble and mobile in the natural water environment, which can result in cancer and other chronic illnesses (Sheng et al., 2016a; Liang et al., 2013, 2014a,b; Li et al., 2014; Liang et al., 2015). So, it is very urgent to immobilize these anions by suitable methods. In view of these literature surveys, there is need for more in-depth study with sorption of anions on titanate nanotube.

Hence, in the present work, we will study the sequestration of selenate (Se(VI) or $SeO_4{}^{2-}$) and selenite (Se(IV) or $SeO_3{}^{2-}$) onto titanate nanotube by a sorption process via a combined classical batch and advanced EXAFS approach. The main objectives of this work are to (i) investigate the sorption behavior of titanate nanotubes towards selenate (Se(VI) or $SeO_4{}^{2-}$) and selenite (Se(IV) or $SeO_3{}^{2-}$) under different solution compositions, (ii) provide a mechanistic description of the sorption process using X-ray absorption fine structure (XAFS).

2. Materials and methods

2.1. Chemicals and materials

All chemicals (including HCl, NaOH, NaCl, Na_2SeO_4, Na_2SeO_3) were purchased in analytical purity and used without any further purification. All solutions were prepared with 18 MΩ cm de-ionized water (Milli-Q Gradient, Millipore, USA). The titanate nanotubes (TNTs) were synthesized by a simple hydrothermal procedure from TiO_2 particles, which has been described in our previous reports (Sheng et al., 2014b, 2013b, 2015; Sheng and Hu, 2013).

2.2. Macroscopic and microscopic experiment

All macroscopic interaction experiments of the sequestration of Se(VI) and Se(IV) onto TNTs were conducted in a 100-mL conical flask at ~25 °C in water bath incubator. The suspension of TNT and NaCl solution were pre-equilibrated for 24 h, then Se(VI) or Se(IV) stock solution was added to achieve the desired concentration of different components. The pH was adjusted to the desired value by adding negligible volume of 0.01 mol/L of HCl or NaOH. After the suspensions were shaken for equilibrium, the solid and liquid phases were separated by centrifugation at ~9000 rpm for the determinations of Se(VI) or Se(IV) concentrations. To take into account of Se(VI) or Se(IV) loss expect for TNT adsorption (i.e., Se(VI) or Se(IV) adsorption on conical flask wall), calibration curve was obtained separately under otherwise identical conditions but no adsorbent. Based on the calibration curve, the adsorption (%) of Se(VI) or Se(IV) was expressed,

$$Adsorption(\%) = \frac{C_0 - C_e}{C_0} \times 100\% ,$$

where C_0 is the initial concentration, C_e is the equilibrium concentration.

To collect enough solid products for XAFS analysis, the sample was prepared by mixing Se(VI) solution with TNTs in a 1000-mL conical flask, then, the solid particles were filtered, washed, finally freeze dried. The collected products were stored in N_2 atmosphere to prevent atmospheric contamination. Se K-edge XAFS spectra at 12684.5 eV were recorded at room temperature at Shanghai Synchrotron Radiation Facility (SSRF, China) in fluorescence mode. The electron beam energy was 3.5 GeV and the mean stored current was 300 mA. A superconductor wiggler with a maximum magnetic field B_0 of 6 T inserted in the straight section of the storage ring was used. The energy of X-ray was detuned by using a fixed-exit double-crystal Si (111) monochromator. A multi-element pixel high purity Ge solid-state detector was used to collect the fluorescence signal. Analysis of EXAFS and XANES data was performed using SixPACK software (Newville, 2001) and IFEFFIT (Rehr et al., 1992). The individual scans were averaged followed by linear preedge subtraction, linear background removal, unit step edge normalization, isolation of the $\chi(k)$ function with a cubic spline function, followed by k^3 weighting. Theoretical EXAFS amplitude and phase functions for Se-O, and Se-Ti single scattering paths were then generated by FEFF 7.0 (Ankudinov and Rehr, 1997; Webb, 2005). Fitted parameters such as amplitude reduction factor ($S_0{}^2$), Fermi shift (E_0), interatomic distance (R), and Debye-Waller factor (σ^2) were first established with reasonable guesses and were fitted in k-space. The zeta potential of the obtained suspension was then determined using a zeta potential analyzer (Zetasizer Nano ZS, Malvern Co., UK). SEM and TEM were carried out with H-7500 (Hitachi, Japan). FTIR analysis was performed using a Nexus 670 spectrometer (Thermo Nicolet, Madison) equipped with a KBr beam splitter. N_2-BET adsorption-desorption were determined at 77 K using Micromeritics ASAP 2010 equipment. XRD analysis was performed with Cu K_α radiation (λ= 0.154 nm) on a Rigaku X-ray diffractometer. Se(VI) concentrations were analyzed by Hydride generation atomic absorption spectrometry (HG-AAS, (AA-6300C, Shimadzu)).

3. Results and discussion

3.1. Characterization of TNT surface properties

The main surface properties of TNTs were characterized and the results are shown in Fig. 1. The tubular structure of TNTs with an outer diameter of 10 ~ 30 nm and an inner diameter of 3.5-6.5 nm, as well as a length of a few hundreds nanometers (ranging from