Adsorptive removal of arsenic using a novel akhtenskite coated waste goethite

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A B S T R A C T

In recent years, the synthesis of manganese-based mixed oxides that can promote both the oxidation and the adsorption of arsenic has aroused great interest among those who are involved in management of arsenic wastewater. In this work, waste goethite, BT9 (α-FeOOH, 0.25–1 mm, 232 m^2 g^{-1}), which was recycled from industrial fluidized-bed Fenton equipment, was combined with akhtenskite (ε-MnO$_2$), called MnBT9, for use in the adsorptive removal of arsenic (As(III) and As(V)) from solution. MnBT9 was prepared using a fluidized-bed reactor (FBR) in which ε-MnO$_2$, formed by oxidizing Mn^{2+} with sodium hypochlorite (NaOCl), was uniformly deposited onto BT9 support particles. Langmuir isotherms suggested that BT9 effectively adsorbed As(V) (28.25 mg g^{-1}) but was mostly ineffective in adsorbing As(III) (8.03 mg g^{-1}). Nevertheless, the deposition of MnO$_2$ on MnBT9 markedly increased its capacity to adsorb As(III) (34.36 mg g^{-1}) without significantly influencing the retention of As(V) by the BT9 substrate. K-edge XANES (X-ray absorption near edge structure) analysis revealed that As(III) was totally oxidized to As(V) on MnBT9. A pseudo-second-order model was used to elucidate the kinetics of adsorption; at pH 3.5, MnBT9 removed As(III) at a higher rate than it removed As(V), proving that oxidation was a limiting step of arsenic removal when the BT9 substrate dominated the adsorption of As(V) in either its native form or formed by the oxidation of As(III).

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1. Introduction

Long-term exposure to arsenic, which is known to be a human carcinogen, probably induces several types of cancer in organs, such as the skin, lungs, liver, bladder, kidney and others (Bhattacharjee et al., 2013). In 1993, the World Health Organization (WHO) set a limit of 10 ppb of arsenic in drinking water (which was adopted by Taiwan's Environmental Protection Agency (EPA) in 2001). Arsenic enters the environment due to both natural and anthropogenic means, and exists in four major oxidation states (−3, 0, +3 and +5); the most abundant forms of As in soil and water are inorganic arsenate (As(V), H$_3$AsO$_4$) and arsenite (As(III), H$_3$AsO$_3$) (Gupta and Ghosh, 2009; Chen et al., 2013a). As(V) is stable in aerobic environments and As(III) is often present in anaerobic reducing environments such as

groundwater (Mohan and Pittman Jr. et al., 2008). Uncharged H$_3$AsO$_3$ molecules are present over a wide range of pH values (pH < 9.2), and H$_3$AsO$_4$ dissociates to form anions at pH values of above 2 (H$_2$AsO$_4^-$ at pH 2–7, HAsO$_4^{2-}$ at pH 7–11, AsO$_4^{3-}$ at pH > 11) (Wang and Mulligan et al., 2006). Hence, As(III), which is more toxic and mobile than arsenate As (V), is, unlike As(V), very difficult to remove by conventional physicochemical methods (Smedley and Kinniburgh et al., 2002).
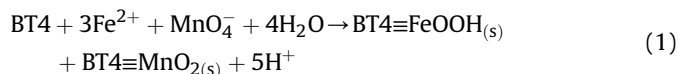
Numerous arsenic remediation methods have been discussed; those of most importance in the 21st century include precipitation, coagulation, membrane, ion-exchange and adsorption (Mohan and Pittman Jr. et al., 2008; Kim and Benjamin et al., 2004; Balasubramaniana et al., 2009; Harisha et al., 2010; Kobya et al., 2011; Tongamp et al., 2010; Bordoloi et al., 2013). Among methods for removing arsenic, adsorption is the most widely utilized because it is simply implemented and cost-effective. Iron oxides, including amorphous hydrous ferric oxide (FeO(OH)), goethite (α-FeOOH) and hematite (α-Fe$_2$O$_3$), are the most promising adsorbents for the removal of As(III) and As(V) from water owing to their high affinity for inorganic arsenic species (Gupta et al., 2009; Simeonidis et al., 2011; Aredes et al., 2013; Tresintsi

et al., 2014; Bulut et al., 2014). The synthesized iron oxides typically have a high specific surface area, and therefore a large capacity of arsenic. The mean nano-to micrometer sizes of iron oxide particles leads to the need for inconvenient additional separation, which may even result in secondary pollution in practice. Iron oxide-coated sand has been developed as an adsorbent for removing arsenic (Thirunavukkarasu et al., 2003; Rahman et al., 2013; Aredes et al., 2013), but as the level of iron in such sand-based adsorbents is reduced, the number of active sites for the adsorption of arsenic decreases dramatically.

Adsorption methods that are generally effective for As(V) are sometimes ineffective for As(III), and an oxidation step is necessary to eliminate considerable amounts of As(III). Oxidants of As(III) include hypochlorite, chlorine dioxide, monochloramine, permanganate and manganese dioxide (Driehaus et al., 1995; Sorlini and Gialdini, 2010). Manganese dioxide is an active oxide that is abundant in the environment, and has been studied intensively as an adsorbent, oxidant, catalyst, and capacitor owing to the severe defects in its structure (Kuan and Chan, 2012). Mn in manganese dioxide has three oxidation states, +2 to +4, and so can act as an oxidant of As(III) (Driehaus et al., 1995). Recent reports have investigated the binary oxides, which can acting as oxidants and adsorbents of As(III), in many metal composites (Gupta et al., 2009, Basu and Ghosh et al., 2011; Huang et al., 2011a; Tu et al., 2013). A common route for preparing the composite of manganese dioxide and iron oxide involves the co-precipitation of manganese and ferric hydroxides (Zhang et al., 2007; Gupta et al., 2010; Singh et al., 2010). In the authors' earlier works, an iron oxide-based adsorbent, MnBT4, was prepared, and on it, permanganate was reduced by ferrous ion and deposited as manganese dioxide, for removing As(III) (Huang et al., 2011a).

$$\begin{aligned} BT4 + 3Fe^{2+} + MnO_4^- + 4H_2O \rightarrow BT4{\equiv}FeOOH_{(s)} \\ + BT4{\equiv}MnO_{2(s)} + 5H^+ \end{aligned} \quad (1)$$

The iron oxides of the BT series, which were granular goethite (α-FeOOH), were solid wastes that were collected from real fluidized-bed Fenton instruments. The Fenton process is utilized in the long-term treatment of organic wastewater, and one of its byproduct, iron hydroxide, can be homogeneously crystallized to form granular particles of half to several millimeters in diameter (Huang et al., 2011b). Thus, the problem of solid–liquid separation that is encountered using the dispersed nanoparticles was mitigated using BT iron oxide.

The efficiency of removal of As(III) by MnBT4 was around 15% higher than that by BT4 (Huang et al., 2011a). The authors have attributed the moderate effect of the MnO_2 deposited on As(III) adsorption to the low efficiency of loading MnO_2 by the reduction of permanganate; no more than 0.1 wt% of manganese dioxide was deposited on MnBT4, and hence the efficiency of oxidation and adsorption of arsenite were limited. In this work, another batch of recycled BT, called BT9, was used as the adsorbent. To overcome the limited loading of MnO_2 by deposition on BT4 via a reaction of ferrous ion and permanganate, the manganese ions (Mn(II)) were oxidized by active chlorine to form MnO_2-coated BT9, MnBT9, in a laboratory-scaled fluidized-bed reactor (FBR). Factors, such as the concentration of hypochlorite and pH, which influence coating with MnO_2 were investigated. MnBT9 was utilized to elucidate the exact behavior associated with the adsorption of arsenic in water. The capacities of MnBT9 to adsorb As(III) and As(V) were obtained by fitting the experimental data using isotherm models, and their kinetics were examined with reference to the pseudo-second order rate equations.

2. Materials and methods

2.1. Materials

Sodium hypochlorite (NaOCl, 12 wt%), used for generating hypochlorite acid, HOCl, was supplied by Nihon Shiyaku Industries (JAPAN). Manganese sulfate monohydrate, $MnSO_4 \cdot H_2O$, used to produce the stock solution of Mn(II), was obtained from J. T. Baker Chemical Co. (US). The synthetic As(III) and As(V) wastewaters were prepared using sodium arsenite ($NaAsO_2$) and trisodium arsenate heptahydrate ($Na_3AsO_4 \cdot 7H_2O$), respectively, which were purchased from Kanto Chemical Co. Inc. (JAPAN). All chemicals were of analytical grade and used without purification.

All solution samples in the FBR process and the adsorption experiments were diluted with deionized water (resistivity >18.3 MΩ) that had been purified using an RO-ultrapure system. The BT9 iron oxide that supported manganese dioxide and was used to adsorb arsenic was a byproduct of the treatment of tannery effluent wastewater from a fluidized-bed Fenton instrument (Huang et al., 2011b). Table 1 presents the characteristics of BT9. The Brunauer–Emmett–Teller (BET) surface area, total pore volume, and mean pore diameter were measured using a surface area/porosity analyzer (Micromeritics ASAP). X-ray crystallography (XRD, Rigaku RX III, Japan) was used to identify the structures of the manganese and iron oxide, whose surface morphology was observed by scanning electron microscopy (SEM, JEOL JSM-6700F, Japan).

2.2. Preparation of MnBT9

A laboratory-scale fluidized bed reactor (FBR) described in the authors' earlier investigation was utilized to synthesize MnBT9 (Huang et al., 2011a). The FBR was a glass column with an internal diameter of 2 cm, a total height of 80 cm and a volume of 550 mL. The stock solutions, 10 mM $MnSO_4$ and NaOCl in a specific molar ratio to Mn(II), conditioned to pH 5.5 by the addition of H_2SO_4, were prepared as the two inlet compounds. BT9 particles were loaded in the FBR, which was maintained at 50% expansion by controlling the upstream flow rate: both input rates of Mn(II) and NaOCl were 8 ml min^{-1}, and the reflux rate was 30 ml min^{-1}. The reaction solutions were recirculated in the batch experiments. After a specific interval, the Mn concentration in the sample of the effluent was analyzed using an atomic analysis spectrometer (AAS, SensAA Dual). The final MnBT9 sample was dried at 105 °C for 4 h and stored in a desiccator for subsequent use.

2.3. Arsenic adsorption experiments

Batch experiments on arsenic adsorption were conducted using a Jar-Test apparatus at room temperature. 1–10 g masses of BT9 and MBT9 particles were mechanically stirred (100 rpm) with arsenic solutions (1000 mL) that had an initial concentration of 10 ppm-As(III)/(V). For the purpose of adsorbing anionic arsenic,

Table 1
Characterization of BT9 adsorbent.

Properties	
Particle size	0.25–1 mm
Apparent density	2.59 g cm^{-3}
Bulk density	1.56 g cm^{-3}
BET specific surface area	232 m^2 g^{-1}
Average pore size	44 nm
Pore volume	0.24 cm^3 g
Iron content	68.3 wt%