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# Efficient removal of trace arsenite through oxidation and adsorption by magnetic nanoparticles modified with Fe–Mn binary oxide

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## ABSTRACT

Magnetic nanoparticles (MNPs) modified simultaneously with amorphous Fe and Mn oxides (Mag-Fe–Mn) were synthesized to remove arsenite [As(III)] from water. Mag-Fe–Mn particles were fabricated through heterogeneous nucleation technique by employing the maghemite as the magnetic core and Fe–Mn binary oxide (FMBO) as the coating materials. Powder X-ray diffraction, X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and transmission electron microscopy were utilized to characterize the hybrid material. With a saturation magnetization of 23.2 emu/g, Mag-Fe–Mn particles with size of 20–50 nm could be easily separated from solutions with a simple magnetic process in short time (within 5 min). At pH 7.0, 200 µg/L of As(III) could be easily decreased to below 10 µg/L by Mag-Fe–Mn particles (0.1 g/L) within 20 min. As(III) could be effectively removed by Mag-Fe–Mn particles at initial pH range from 4 to 8 and the residual As was completely oxidized to less toxic arsenate [As(V)]. The co-occurring redox reactions between Mn oxide and As(III) was confirmed by XPS analysis. Chloride, sulfate, bicarbonate, and nitrate at common concentration range had negligible influence on As(III) removal, whereas, silicate and phosphate reduced the As(III) removal by competing with arsenic species for adsorption sites. As(III) removal was not obviously affected by natural organic matter (up to 8 mg/L as TOC). Mag-Fe–Mn could be regenerated with ternary solution of NaOH, NaCl, and NaClO. Throughout five consecutive cycles, the adsorption and desorption efficiencies maintained above 98% and 87%, respectively. Mag-Fe–Mn had a larger adsorption capacity for As(III) (47.76 mg/g) and could remove trace As(III) more thoroughly than MNPs modified solely with either Fe or Mn oxide due to the synergistic effect of the coating Fe and Mn oxides. This research extended the potential applicability of FMBO to a great extent and provided a convenient approach to efficiently remove trace As(III) from water.

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## 1. Introduction

Arsenic in groundwater has attracted extensive attention since long-term ingestion of arsenic-contaminated water could result in cancer and other severe health problems

(Bissen and Frimmel, 2003a). Consequently, regulations on arsenic concentration limit for drinking water has become increasingly strict. Most countries are implementing maximum contaminant level (MCL) of 10 µg/L recommended by the World Health Organization (WHO). Soluble arsenic in

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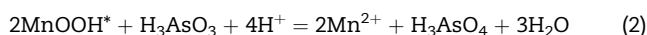
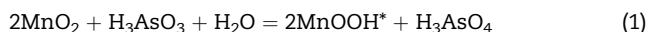
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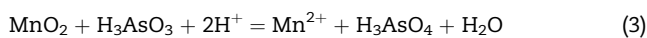
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natural waters exists in two predominant species, i.e. arsenate [As(V)] and arsenite [As(III)]. The predominant chemical state of arsenic in groundwater is usually As(III) (Smedley and Kinniburgh, 2002). For example, Chang et al. (2010) reported that As(III) accounted for 80% of the total arsenic content in a groundwater sample collected from Beijing suburb. More importantly, As(III) is 25–60 times more toxic than As(V) (Korte and Fernando, 1991) and therefore deserves more attention.

Adsorption is one of the most promising approaches to remove arsenic from water. Ferric (hydr)oxides are highly preferred for As(V) removal (Pierce and Moore, 1982; Raven et al., 1998). However, the removal of As(III) is less effective relative to As(V). Thereby, an oxidation pretreatment is usually employed to convert As(III) into As(V) prior to adsorption (Bissen and Frimmel, 2003b). Manganese oxides are extensively used as the oxidizing agent. The reaction proceeds stepwise as Eqs. (1) and (2) (Nesbitt et al., 1995):



where MnOOH\* represents an intermediate product composed of Mn(III), hydroxyl and H<sub>2</sub>O. Hence the overall reaction can be expressed as Eq. (3):



Recently, an integrated material named Fe–Mn binary oxide (FMBO) was synthesized and proved to be highly efficient for As(III) removal (Zhang et al., 2007b). The material was composed of amorphous Fe(III) and Mn(IV) oxide, and thus could combine the oxidation and adsorption processes (Zhang et al., 2007b). However, it is difficult to recycle FMBO from the suspension after treatment, especially when FMBO is well dispersed into the water as nanoparticles. Magnetic nanoparticles (MNPs) were found to have great potentials for cyclic utilization due to their convenient separation from water. Nevertheless, bare MNPs such as magnetite might not be able to efficiently remove As(III) due to smaller adsorption capacity and lower bonding affinity in comparison with ferric (hydr) oxides (Giménez et al., 2007).

Therefore, it can be expected that MNPs modified with FMBO not only could effectively remove As(III) but also would be easily separated from solution. Materials with quite similar structures have been fabricated very recently. Silva et al. (2012) developed a magnetic composite of Fe<sub>3</sub>O<sub>4</sub> and Mn<sub>3</sub>O<sub>4</sub>, whose adsorption capacity for As(III) was found to be 14 mg/g at 25 °C and pH 5.0. Zhao et al. (2012) synthesized novel Fe<sub>3</sub>O<sub>4</sub>–MnO<sub>2</sub> core-shell structured nanoplates with more significant adsorption capacity. However, the shell parts of these materials were predominantly Mn oxides instead of FMBO. Actually, the other essential constituent of FMBO, i.e. amorphous Fe(III) oxide, has strong affinity with As(V) (Pierce and Moore, 1982; Raven et al., 1998; Zhang et al., 2007a). Moreover, these studies examined As(III) adsorption behaviors at pH 5.0 and the initial As(III) concentrations were at mg/L level. Further investigations into trace As(III) removal under

chemical circumstances close to actual groundwater is still required.

To our best knowledge, MNPs modified simultaneously with amorphous Fe and Mn oxides has never been fabricated and utilized to remove trace As(III) from water. Hence, this research is aimed to fabricate a novel material, i.e. MNPs modified with FMBO and to investigate the mechanism of As(III) removal. This study mainly focused on the removal of As(III) at low initial concentration (200 µg/L) and neutral pH (7.0). Meanwhile, the effects of pH, common coexisting anions, and natural organic matters (NOM) on As(III) removal were also examined. Stability of the prepared adsorbent (reflected by Fe and Mn release levels after treatment) and the feasibility of cyclic reuse were also taken into consideration.

## 2. Materials and methods

### 2.1. Materials

As(III) stock solutions were synthesized by dissolving NaAsO<sub>2</sub> (Xiya Reagent, Chengdu, Sichuan, China) of analytical grade with ultrapure water (resistivity >18.2 MΩ cm) from an integral water purification system (Milli-Q, Millipore, Billerica, MA, USA). Humic acid sodium salt (Acros Organics, Geel, Belgium) and alginic acid sodium salt (Aldrich, St. Louis, MO, USA) were selected to represent typical natural organic matters (NOM). Commercially available Fe<sub>3</sub>O<sub>4</sub> (nanopowder, particle size <50 nm, Aldrich, St. Louis, MO, USA) was employed for comparative purpose. Other chemicals were of analytical grade from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and Xilong Chemical Group (Shantou, Guangdong, China). Standard solutions for analytical use were purchased from National Institute of Metrology of China and were diluted to desired concentrations with ultrapure water.

### 2.2. Adsorbent preparation

The proposed adsorbent was fabricated via a two-step process including preparation of the magnetic cores and modifying them with FMBO. A conventional co-precipitation method was adopted to prepare the magnetic core under facile conditions. At room temperature, 2 M NaOH solution was added dropwise into a 500-mL three-neck round flask containing 200 mL of binary solution of 0.15 M FeCl<sub>3</sub> and 0.10 M FeSO<sub>4</sub> under vigorous non-magnetic agitation until the pH reached 10 when the black precipitate emerged. After the maintenance under vigorous agitation for another 30 min, the precipitate was separated from the suspension by a magnet and washed repeatedly with deionized water until neutral pH of the supernatant was observed. Thus, the magnetic core of the adsorbent was obtained and was then re-dispersed with 200 mL of deionized water by exposure to ultrasonic wave for 2 min. The modification of the magnetic particles was implemented via a heterogeneous nucleation process inspired by Hong et al. (2008). Specifically, 1 mL of polyethylene glycol (PEG) 400 was first added into the flask. Under vigorous agitation, 50 mL of precursor solution (binary solution comprised of 0.6 M FeCl<sub>3</sub> and 0.3 M MnSO<sub>4</sub>) and 50 mL of precipitant solution (3 M NaOH) were simultaneously pumped through separate

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