



Redox transformation of arsenic by magnetic thin-film MnO₂ nanosheet-coated flowerlike Fe₃O₄ nanocomposites



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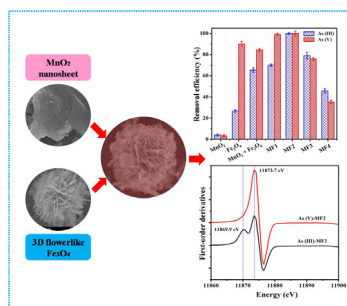
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HIGHLIGHTS

- Magnetic MnO₂ nanosheet-coated flowerlike Fe₃O₄ nanocomposites were synthesized.
- The ratio of Mn/Fe was a key factor influencing the uptake of arsenic in aqueous solution.
- Redox transformation of arsenic in liquid-solid phase were simultaneously explored.
- MnO₂ acted as an oxidant, while Fe₃O₄ played the role as arsenic species adsorbent.

GRAPHICAL ABSTRACT



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ABSTRACT

Inorganic arsenic cycling in the natural environment is significantly controlled by manganese/iron oxides, and studying the redox transformation of arsenic in both aqueous and solid phase is therefore essential to understand its environmental toxicity and predict its environmental behavior. Herein, the synthesized magnetic thin-film MnO₂ nanosheet-coated flowerlike Fe₃O₄ nanocomposites have been used to simultaneously investigate the potential redox transformation of arsenic in aqueous phase and arsenic speciation on the solid phase interface. The results showed the initial Mn/Fe ratio has serious influenced the morphologies, textural properties and uptake of arsenic in aqueous solution. The maximum adsorption capacities of As(III) and As(V) by MF2 were 76.73 mg/g and 120.50 mg/g, respectively. After 10 h reaction, the total arsenic concentration in both As(III)-MF2 system and As(V)-MF2 system far below than that of 10 µg/L, which was setted the maximum guideline concentration value in drinking water by World Health Organization (WHO). HPLC-ICP-MS revealed that in aqueous solution part of As(III) was oxidized into As(V), while As(V) was not reduced into As(III). X-ray absorption near edge structure (XANES) and XPS analysis from solid phase further confirmed that the MnO₂ nanosheet mainly acted as an oxidant, while flowerlike Fe₃O₄ only played the role as an arsenic species adsorbent. Extended X-ray absorption fine structure (EXAFS) analysis indicated that both As(III) and As(V) formed inner-sphere bidentate binuclear corner-sharing (²C) complexes with an As-Fe interatomic distance of 3.32–3.34 Å on the interface of As-MF2 solid phase.

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1. Introduction

Arsenic is a toxic metalloid widely distributed in atmosphere, soil and water, and arsenic contamination in natural water is a

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global threat due to its higher toxicity and carcinogenicity [1,2]. Typically, the predominant forms of arsenic in aqueous environment are arsenite and arsenate [3,4], which depend significantly on pH and redox conditions [5]. Understanding the abiotic redox transformation of arsenic between arsenite and arsenate is necessary due to their different physical and chemical properties, which determines its environmental toxicity and fate. In addition, ingesting arsenic-contaminated water could cause many diseases, which extremely detrimental to human healthy [6–9]. Thus, the World Health Organization (WHO) has set a stringent limit of 10 $\mu\text{g/L}$ for arsenic in drinking water [10]. Therefore, effective removal of arsenic has becoming more and more urgent in water environment. The reactions between arsenic and iron (hydr)oxides play a very important role in these inorganic arsenic species mobility, stability and potential bioavailability, which commonly occurs in the aquatic environment. Nevertheless, these iron (hydr)oxides remove effectively on the arsenate and often not the arsenite, which is the thermodynamically stable form and is presented as non-ionic form of H_3AsO_3 at neutral pH [11]. Recently studies have focused on arsenic immobilization by Fe–Mn bimetal oxides, since these iron manganese binary oxides not only show obviously synergistic effect compared with the individual parents metal oxides, but also exhibit a dual function role during the process of As(III) removal [6,12,13]. Furthermore, iron and manganese elements have similar chemical properties and often exist together in soils, minerals and sediments, which play an important role in arsenic redox transformation and retention at oxic-anoxic boundary in natural environment [14–16].

Macroscopic studies over the last several years have provided valuable insight on the effect of pH value, ionic strength and coexisting ions on arsenic removal by iron-based bimetal oxides. However, currently research also indicated that the morphologies and textural properties of materials affected arsenic uptake significantly compared with their bulk counterparts [17–19]. In addition, simultaneously analysis the redox transformation of arsenic species in aqueous phase and arsenic speciation on the solid interface of bimetal materials from microscopic aspects has yet to be investigated. Since the redox transformation and speciation of the metalloid arsenic determine its environmental fate and toxicity. X-ray photoelectron spectroscopy (XPS) is often used to investigate the composition and chemical state of arsenic on solid phase, however, it is usually conducted in ultrahigh vacuum and has a probing depth limited to approximately 10 nm beneath the sample surface. Additionally, due to the fact that the photoelectrons are attenuated to different extents with depth, absolute quantification of arsenic species distributed heterogeneously throughout the sampling depth is complicated [20]. Fortunately, synchrotron-based X-ray absorption spectroscopic (XAS), including X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS), commonly allows for analysis on the environmental behavior of arsenic on the speciation level to overcome these limitations [20,21]. This XAS not only determine the oxidation state of the adsorbed ions, but also directly provide information about the coordination number and the interatomic distances of nearest/next-to nearest neighbors, which obviously identified the local structure of the adsorbed ions [22,23]. Nevertheless, these solid phase investigations are mostly focusing on pure iron (hydr)oxides or manganese oxides [24,25], and few information is available on manganese iron bimetal oxides. In addition, some disputable results and conflicting reports on the molecular level mechanism of arsenic removal occurred even used the same materials. Jönsson indicated that both As(III) and As(V) formed the bidentate binuclear corner-sharing complexes (^2C complexes) on the surface of Fe_3O_4 from EXAFS spectra analysis [26], while Wang and Morin suggested that formation of a tridentate As(III) inner-sphere complexes (^3C complexes) and As(V) formed ^2C complexes on the sur-

face of Fe_3O_4 nanoparticles, respectively [27–29]. It is very necessary to investigate the arsenic binding modes because different binding modes contribute to the differences in arsenic immobilization [30]. From XANES spectra data, Ona-Nguema reported that the rapid oxidation of As(III) to As(V) on the surface of magnetite due to the dissolved oxygen [15], however, both Chowdhury and Liu claimed that the reduction of adsorbed As(V) to As(III) on nanoscale magnetite surface was occurred [31,32], this potential reductive transformation of As(V) to As(III) should be gained more attention in both aqueous solution and solid phase because As(III) has more toxicity, mobility and solubility compared with As(V) [7]. Those above investigations are mostly focusing on solid phase and without considering the redox transformation of arsenic species in aqueous, meanwhile, iron-based bimetal oxides seem to be more complicated compared with pure iron oxides. Therefore, it is very essential to simultaneously investigate the potential redox transformation in aqueous and arsenic speciation on the surface of bimetal materials along with the interaction between them to understand comprehensively the behaviors and mechanisms of arsenic removal by manganese iron bimetal oxides.

Accordingly, in this study we report a facile method for synthesizing magnetic MnO_2 nanosheet-coated 3D flowerlike Fe_3O_4 nanocomposites. The objectives of this work were to (1) characterize the morphologies, textural and magnetic properties of manganese iron bimetal oxides (MFs) with different initial ratios of Mn/Fe, (2) explore the effect of Mn/Fe ratio on As(III) and As(V) removal in aqueous solution, (3) simultaneously investigate the potential redox transformation of arsenic in aqueous phase and arsenic speciation on the solid phase interface of manganese iron bimetal nanocomposites using High Performance Liquid Chromatography-Inductively Coupled Plasma-Mass Spectrometry (HPLC-ICP-MS), X-ray absorption spectroscopic (XAS) and X-ray photoelectron spectroscopy (XPS), which shed light on the mechanisms of arsenic removal by manganese iron bimetal oxides.

2. Experimental section

2.1. Synthesis of 3D flowerlike Fe_3O_4 nanostructures

In a typical experiment, 1.2 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 7.2 g tetrabutylammonium bromide (TBAB) and 2.7 g urea were dissolved in 180 mL ethylene glycol (EG) in a 250 mL round-bottom flask. The obtained red solution was magnetically stirred and heated to 185 °C. After refluxing for 30 min at 185 °C, the reaction mixture was cooled to room temperature, the precipitate was collected, centrifuged, washed with ethanol several times and dried at 60 °C. The obtained green-yellow powders were heated to 450 °C and calcined at this temperature for 3 h under a high purity nitrogen atmosphere, and the final obtained black powders were 3D flowerlike magnetite nanostructures.

2.2. Synthesis of MnO_2 nanosheet-coated 3D flowerlike Fe_3O_4 nanocomposites

In brief, 20 mL as-prepared 3D flowerlike magnetite solutions (10 mM) was added to the 100 mL 2-(N-morpholin) ethanesulfonic acid (MES) solutions (0.1 M, pH 6.0) in a 250 mL flask, then four different amounts (20, 40, 60 and 80 mL) of KMnO_4 solutions (10 mM) were added to the flasks, respectively. The mixture were sonicated for 40 min, the brownish black precipitation was collected with a permanent magnet, washed with ultrapure water (18.2 $\text{M}\Omega \text{cm}^{-1}$, Millipore) several times and dried at 60 °C overnight. The obtained materials were termed as MF1, MF2, MF3 and MF4, respectively, corresponding to the four different amounts of KMnO_4 solutions. For comparison, pure MnO_2 nanosheet was

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