



Effects of Mn(II) on the sorption and mobilization of As(V) in the presence of hematite

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ABSTRACT

In this study, the effects of Mn(II) on the sorption and mobilization of As(V) by synthetic hematite were investigated. Our results showed that As(V) removal by hematite was evidently dependent on pH, and simultaneous addition of Mn(II) and As(V) into hematite suspension resulted in more removal of As(V) via electrostatic attraction at pH 4.0, 7.0 and 8.3. However, in Mn(II) pre-loaded system, the removal percentages of As(V) at pH 8.3 decreased by 17.0%, 20.7% and 26.7% after 24 h at the aging time of 2, 12 and 36 h, respectively. The concentrations of the released As(V) after the addition of 1 mM Mn(II) were 23.6, 12.9 and 7.0 μM at pH 8.5 in 2, 3 and 4 g L⁻¹ hematite suspension, respectively. But Ca²⁺ did not show such an effect under similar experimental conditions. Abiotic oxidation of Mn(II) on hematite played an important role in As(V) mobilization. The growing thin layer of Mn(III, IV) (hydr)oxides (MnO_x) formed on hematite would take up the sorption sites pre-occupied by As(V) and resulted in the release of the adsorbed As(V) back into solution. This study enriched our understanding on As(V) fate in the coexistence of iron oxides and Mn(II).

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1. Introduction

Arsenic is a toxic contaminant in natural aquatic environments and its toxicity derives from arsenic's affinity to proteins, lipids, and other cellular components [1]. Due to its acute toxicity, the World Health Organization (WHO) has revised the guidelines for maximum contaminant level (MCL) of 10 $\mu\text{g L}^{-1}$ for arsenic in drinking water [2]. In oxygen-rich environments, arsenate [As(V)] is a predominant inorganic species and primarily exists as H₂AsO₄⁻ and HAsO₄²⁻ in natural aquatic environments since the pK_a values for arsenic acid are pK_{a1} = 2.3, pK_{a2} = 6.8, and pK_{a3} = 11.6 [3].

The common oxides of manganese, iron and aluminum are important sorbents for immobilizing arsenic in natural ecosystems [3–7]. The extent of arsenic sorption is strongly influenced by pH and the presence of other dissolved substances that interact with mineral surfaces or arsenic itself [3–9]. When natural organic matter (NOM) and As(V) were mixed together with hematite ($\alpha\text{-Fe}_2\text{O}_3$), NOM dramatically delayed the equilibrium time and reduced the sorption capacity of As(V) [4]. Competition between arsenic and other anion sorbates (i.e. phosphate, silicate, sulfate,

chloride, carbonate, bicarbonate) has also been studied in previous works [5,6,8,10]. As(V) sorption on hydrous ferric oxides (HFO) decreased from 95% to about 80% at pH 4.0 in the presence of phosphate [5]. Although carbonate increased As(V) sorption on hematite in the air-equilibrated systems at pH 4 and 6, and at pH 8 after 3 h of reaction, suppressed As(V) sorption was also observed in the air-equilibrated system in the early stages of the reaction at pH 8 [6]. Cations such as Zn²⁺, Ca²⁺ and Mg²⁺ can enhance the sorption capacity to As(V) [10–12]. Gräfe et al. [11] indicated that As(V) sorption on goethite ($\alpha\text{-FeOOH}$) increased by 29% at pH 4.0 and by more than 500% at pH 7.0 in the presence of Zn(II). Mn(II) is ubiquitous in aquatic environments and its effect on As(V) sorption has not been studied yet.

The adsorbed arsenic can be mobilized in aquatic environments, in which processes such as oxidation, reduction, dissolution and desorption might occur [1,13,14]. Microbes contribute to the mobilization of arsenic adsorbed on iron (hydr)oxides via mediating redox reactions involving As(III) and As(V) or through dissimilatory reduction of insoluble Fe(III) to soluble Fe(II) [15–18]. NOM and anions such as OH⁻, CO₃²⁻, SiO₄⁴⁻ and PO₄³⁻ also accelerate the desorption of As because of competition for sorption sites [1]. However, to the best of our knowledge, there is no published work focusing on the effect of Mn(II) on the mobilization of As(V) adsorbed on iron (hydr)oxides. Previous studies have demonstrated surface catalytic oxidation of Mn(II) on iron

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oxides in the pH range of 7.0–9.0, and heterogeneous oxidation rate of Mn(II) depended on mineral species and increased with the order of γ -FeOOH > α -FeOOH > SiO_2 > δ - Al_2O_3 [19,20]. Junta and Hochella [21] revealed that the top and base of steps on minerals were the most reactive sites for initiating the oxidation reaction of Mn(II), and once the initially adsorbed Mn(II) was oxidized to MnO_x , it became the most reactive sites for continuing the oxidation process, resulting in more MnO_x formation on iron oxides.

In the present study, hematite was selected as a representative iron oxide since it is widely distributed in nature and is an important natural mineral for the sink of trace toxic metal pollutants [4,22,23]. The objectives of this study were to investigate the effects of Mn(II) on the sorption and mobilization of As(V) in the pH range of 4.0–9.0, which is often found in natural aquatic environments. Three parts of experiments were therefore designed: (i) the kinetics of As(V) sorption on hematite in the absence and presence of Mn(II); (ii) the effect of Mn(II) aging (that means Mn(II) pre-loaded on hematite for a long time) on As(V) sorption on hematite; (iii) the effect of Mn(II) on the mobilization of As(V) adsorbed on hematite.

2. Experimental

2.1. Chemicals

Chemicals of analytical grade or higher purity were used without further purification. $\text{NaH}_2\text{AsO}_4 \cdot 7\text{H}_2\text{O}$ (Merck, purity > 99.0%) and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (Tianjin Bodi Chemical Co., Ltd., PR China, purity > 99.0%) were used as As(V) and Mn(II) sources, respectively. Stock solutions of As(V) (5 g L^{-1}) and Mn(II) (0.2 M) were prepared by dissolving the respective salt in deionized water.

2.2. Synthesis and characterization of hematite

Hematite was synthesized by following the method of Schwertmann and Cornell [24]. A beaker containing 1000 mL of 0.002 M HNO_3 was brought into a 98°C vacuum oven overnight. After a brief removal from the oven, 8.08 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were added with vigorous stirring. The bottle was then returned to the oven immediately and held at 98°C for 7 days. The sediment was centrifuged and then washed three times with deionized water. The solid was then dried at 50°C in a vacuum oven for characterization. Morphology of the synthetic hematite was characterized by high-resolution analytical transmission electron microscopy (TEM, Fei Tecnai G2 F20). Fourier transform infrared (FT-IR) spectrum in KBr pellet was conducted on an American Nicolet NEXUS FT-IR spectrometer. Mineralogical composition and purity for synthetic hematite was confirmed using X-ray diffraction (XRD, Rigaku D/max 2200/PC). Fig. 1 shows the XRD pattern of synthetic hematite, in which all diffraction peaks are in good agreement with rhomb-centered hexagonal (rch) hematite (JCPDS Card No. 33-0664). No other peaks were observed, indicating that the as-synthesized sample consists of high-purity, well crystallized hematite nanoparticles. The diameter of the synthetic hematite was about 20–30 nm as shown in TEM analysis (Fig. 2a). The two dominant bands at about 464 cm^{-1} and 545 cm^{-1} in Fig. S1 also indicated the characteristic peaks of crystalline hematite [24], and 3427 cm^{-1} and 1630 cm^{-1} bands suggested the stretching vibration of hydroxyl groups and bending vibration of water molecules, respectively [25]. Specific surface area of synthetic hematite was $40.1 \text{ m}^2 \text{ g}^{-1}$ as determined by BET- N_2 sorption method. The pH of point of zero charge (pH_{pzc}) of synthetic hematite in 0.1 M NaCl solution was 8.9, as determined by potentiometric titration under the atmosphere of pure N_2 [26].

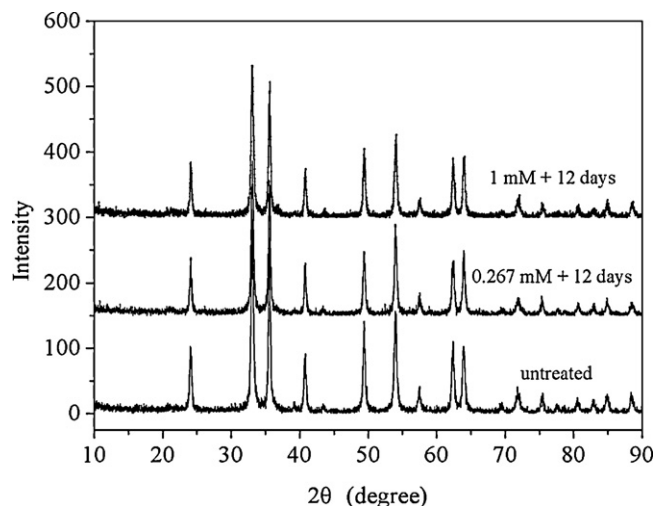


Fig. 1. XRD analysis of synthetic hematite untreated and treated with 0.267 and 1 mM Mn(II) for 12 days at pH 8.3. Hematite concentration was 2 g L^{-1} with working volume 150 mL in 0.1 M NaCl at $25 \pm 0.1^\circ\text{C}$.

2.3. Batch experiments

Compared with dry solid powder, the as-synthesized hematite in wet format could offer a greater surfaces area, owing to their good dispersion and little aggregation characters in water solution. The concentrated hematite was therefore used in all batch experiments. However, concentration of hematite was still expressed in dry weight. The ratio of wet weight to dry weight was determined by placing measured weights of wet samples in the vacuum oven at 50°C to constant value, and its ratio in the present study was 17.6 mL g^{-1} for hematite. Different pH values were maintained with different buffer solutions. Mixture of acetic acid and sodium acetate were only used at pH 4.0 [14 mM acetic acid + 8.3 mM sodium acetate]. Mixture of MOPS (3-morpholinopropane-1-sulfonic acid), sodium borate and/or boric acid were used at pH 7.0, 8.3 and 8.5 [(pH 7.0, 6 mM MOPS + 1.8 mM sodium borate), (pH 8.3, 2 mM MOPS + 4.7 mM sodium borate + 0.67 mM boric acid), and (pH 8.5, 2 mM MOPS + 5 mM sodium borate)].

2.3.1. Sorption of As(V) on hematite in the absence and presence of Mn(II)

Individual sorption of As(V) and simultaneous sorption of As(V) and Mn(II) by hematite were investigated. Hematite was hydrated in 50 mL of 0.1 M NaCl solution at pH 4.0, 7.0 and 8.3 for 4 h to reach equilibrium before the addition of As(V) and Mn(II). After that, 100 mL solution contained As(V) mixed thoroughly with the hydrated hematite suspension with the identical pH values. Mn(II) stock solution was then immediately added into the suspension. The concentrations of Mn(II) and As(V) were 0.267 mM and hematite was 2 g L^{-1} , respectively. Samples were then placed on a shaker at 140 rpm. During the experiments, 1.3 mL samples were taken out regularly and centrifuged at 13,000 rpm for 5 min. The supernatant was used to determine the concentration of As(V) and the average value was recorded.

2.3.2. Effect of Mn(II) aging on As(V) sorption on hematite

To investigate the effect of Mn(II) aging on As(V) sorption in the presence of hematite, different intervals (i.e. 2, 12 and 36 h) of pre-loaded Mn(II) on hematite at pH 8.3 was prepared, followed by the addition of As(V). Both concentrations of Mn(II) and As(V) were 0.267 mM. Samples were placed on a shaker with the same operational conditions as mentioned above. The supernatant was

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