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Defective magnesium ferrite nano-platelets for the adsorption of As(V): The role of surface hydroxyl groups[☆]

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ABSTRACT

In this work, magnesium ferrite (MgFe₂O₄) nano-platelets with rich defects and abundant surface hydroxyl groups were synthesized, and used for the removal of low concentration As(V) in aqueous solution. Results from scanning electron microscopy (SEM) showed that the as-synthesized MgFe₂O₄ nano-platelets were consisted of many individual nanospheres. Rietveld refinement of X-ray diffraction (XRD) data indicated that the Mg²⁺ ions substituted the Fe³⁺ ions at both the octahedral and the tetrahedral sites of the crystal structure. Batch adsorption experiment showed that the equilibrium concentration of As(V) could be reduced down to 4.9 μg·L⁻¹ when the initial concentration of As(V) is 1 mg·L⁻¹, which complied with the drinking water standard of WHO (10 μg·L⁻¹). The adsorption capacity of synthesized MgFe₂O₄ towards As(V) was higher than commonly used iron oxide adsorbents (Fe₃O₄, γ-Fe₂O₃ and α-Fe₂O₃). Mechanistic studies proved that the superior adsorption capacity was attributed to: (1) increased amount of surface hydroxyl groups that resulted from the surface defects. (2) formation of tridentate hexanuclear surface complexes instead of bidentate binuclear complexes, and (3) formation of excess Mg-OH surface hydroxyl groups and As-Mg monodentate mononuclear surface complexes. This work disclosed the correlation of the superior As(V) adsorption ability with the surface hydroxyl groups in defective MgFe₂O₄, and propose MgFe₂O₄ as a potential candidate for the remediation of As-contaminated water.

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1. Introduction

It is commonly known that inorganic arsenic (As) compounds are highly carcinogenic, and many studies are focusing on their removal (Jomova et al., 2011; Gomaa et al., 2017). Magnetite (Fe₃O₄) is an appealing agent for the removal of As because of its outstanding magnetism, large surface area, and strong affinity to As (Liu et al., 2015a; Wang et al., 2014). However, under aerobic condition, Fe₃O₄ can easily be oxidized to other iron oxides/hydroxides that have lower adsorption ability to As, such as maghemite (γ-Fe₂O₃), lepidocrocite (γ-FeOOH), etc. (Wang et al., 2014; Guo and Barnard, 2013). Previous studies showed that the Fe atom in Fe₃O₄ can be replaced by other metal elements (e.g., Mg, Al, Zn, Mn

etc.) to form spinel ferrite (Sickafus et al., 1999). The spinel ferrite is isostructural to Fe₃O₄ and thus retains many physical and chemical properties of Fe₃O₄ (Reddy and Yun, 2016). Moreover, the nanoparticles of the spinel ferrite are much more resistant to oxidation and have abundant defects on the surface that can serve as active sites for As adsorption (Reddy and Yun, 2016).

Previous mechanistic studies revealed that the adsorption of As(V) oxyanion on spinel ferrite was dominated by the process of ligand exchange with surface hydroxyl groups (–OH) to form inner-sphere or outer-sphere complexes (Kumar et al., 2014). Studies on As adsorption by MnFe₂O₄, CoFe₂O₄, and Mg_{0.27}Fe_{2.5}O₄ showed that, the superior As(V) adsorption ability of spinel ferrite than Fe₃O₄ to could be attributed to the presence of abundant hydroxyl groups (Mnfe et al., 2010; Tang et al., 2013). The hydroxyl groups could be formed through the dissociative adsorption of water molecule at the defect sites, and the defects could be formed when a lighter metal ion substituted the Fe atom in Fe₃O₄ (Reddy and Yun, 2016; Sakai et al., 2001). However, not all elements atoms could increase the amount of surface hydroxyl groups in Fe₃O₄ after

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such substitution. For example, although Ni^{2+} substitution greatly increased the concentration of surface hydroxyl groups in Fe_3O_4 , V^{3+} and Co^{2+} were unable to do (Liang et al., 2013; Liang et al., 2015). Compared with other divalent metal ions, magnesium is worth further investigation since it is an abundant and nontoxic alkaline earth metal. It was previously reported that Mg doped γ - Fe_2O_3 ($\text{Mg}_{0.27}\text{Fe}_{2.5}\text{O}_4$) outperformed iron oxides in removing As(V) (Tang et al., 2013). However, the benefits of using Mg to substitute Fe to prepared nano-sized Mg-doped spinel ferrite for As(V) removal remain to be explore.

Theoretically, the formation of new hydroxyl groups is closely associated with the site of the doping atom. In the spinel structure of Fe_3O_4 , one-quarter of the tetrahedral (T_d) and one-half of the octahedral (O_h) sites are filled by iron (Coker et al., 2006). It was found that in Al-, Cd- and Zn-doped substitution Fe_3O_4 , the doping atom preferentially substituted Fe at the T_d site rather than the O_h site (Sickafus et al., 1999; Schwertmann and Murad, 1990; Mathew and Juang, 2007). However, this is not the case for magnesium ferrite (MgFe_2O_4). A recent review showed that in, Mg^{2+} occupied the O_h sites, thus forming an inverse spinel structure (Sickafus et al., 1999). Another report showed that Mg^{2+} could also occupy the T_d sites in to MgFe_2O_4 to form a mixed spinel structure (Yaremchenko et al., 2011). Therefore, the atomic occupancy and distribution of Mg in magnesium ferrite still need to be further clarified.

Compared with Fe_3O_4 , MgFe_2O_4 has the same crystal structure but is more stable. Substituting Mg for Fe in the iron oxide matrix mat induce defects and provide a superior adsorbent to remove As(V) from aqueous. Therefore, in this work, nanostructured spinel MgFe_2O_4 was prepared and its adsorption performance for As(V) was studied. The main objectives of this work are (1) studying the occupancy of Mg atoms in the crystal structure of MgFe_2O_4 ; (2) quantifying the As(V) adsorption ability of MgFe_2O_4 in low concentrations; (3) studying the formation mechanism of surface hydroxyl groups on MgFe_2O_4 . The role of the surface hydroxyl groupson MgFe_2O_4 during As(V) adsorption was examined and rationalized. This study will provide an important theoretical basis on the interaction between As(V) and spinel ferrite, which would further promote the arsenic removal in practical applications.

2. Materials and methods

Chemicals. All chemicals and reagents were of analytical grade and used directly without further purification. The crude materials, including magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), iron nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and ammonium bicarbonate (NH_4HCO_3), as well as anhydrous ethanol ($\text{C}_2\text{H}_5\text{OH}$), which was used as a solvent, were purchased from Chemical Reagent Co., Ltd. (Beijing, China). The stock solutions of As(V) were prepared by dissolving $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ in deionized water.

Synthesis of MgFe_2O_4 spinel. The MgFe_2O_4 sample was prepared by a modified “solvent-deficient” method (Smith et al., 2014). Specifically, a mixture of magnesium nitrate, iron nitrate and ammonium bicarbonate (molar ratio 1: 2: 8) was finely ground in a mortar with a pestle. Grinding was carried out for 15–30 min inside a fume hood until bubbling/popping subsided. The residue was washed with ethanol/deionized water for several times, and the solids were collected after centrifugation, calcined at 350°C for 3 h in air, then cooled down naturally to room temperature to give the MgFe_2O_4 sample.

Batch adsorption experiments. All experiments were run at room temperature and in open air. The adsorption isotherms of As(V) were measured at pH 7.0 ± 0.1 by HCl (0.1 mol L^{-1}) and NaOH (0.1 mol L^{-1}) solution in 50 mL flasks. The dosage of adsorbent was fixed at 0.5 g L^{-1} and the initial concentration of As(V) was varied over $1\text{--}10 \text{ mg L}^{-1}$. The suspension was stirred at 200 rpm for 2 h

before it was passed through a $0.22 \mu\text{m}$ filter, and the concentration of As(V) in the solution was measured by inductively coupled plasma mass spectrometry (ICP-MS). The adsorbent was then separated via centrifugation at 8000 rpm.

The adsorption capacity (q_e) for As(V) was calculated by Equation (1):

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (1)$$

where q_e is the adsorption capacity at equilibrium ($\text{mg} \cdot \text{g}^{-1}$), C_0 and C_e are the initial and equilibrium concentration of As(V) in the solution ($\text{mg} \cdot \text{L}^{-1}$), respectively, V is the volume of the As(V) solution (L), and m is the mass of the adsorbent (g).

The adsorption isotherm was fitted to both the Langmuir model (Equation (2)) and the Freundlich model (Equation (3)):

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{k_l q_m} \quad (2)$$

$$q_e = k_f C_e^{1/n} \quad (3)$$

where q_m (mg/g) represents the maximum adsorption capacity, k_l ($\text{L} \cdot \text{mg}^{-1}$) is the Langmuir constant that represents the affinity between the solute and adsorbent, k_f is the Freundlich constant, and n^{-1} is the adsorption intensity ($1 < n < 10$).

Adsorption kinetics experiments were performed in triplicate with mechanical stirring at 200 rpm. The adsorbent (1 g L^{-1}) was added into the As(V) solutions (5 mg L^{-1} , initial pH = 7.0 ± 0.1), and aliquots (3 mL) were taken from the suspension at designated times (5, 15, 30, 60, 90 and 120 min). The aliquots were centrifuged to collect the supernatant and the precipitate. The supernatant was passed through a $0.22 \mu\text{m}$ filter and the concentration of As(V) in the filtrate was measured by ICP-MS. The data were fitted to the pseudo first-order (Lagergren, 1898) equation (Equation (4)) and the pseudo second-order (Ho and McKay, 1999) equation (Equation (5)):

$$q_t = q_e \left(1 - e^{-k_1 t} \right) \quad (4)$$

$$q_t = \frac{q_e^2 K_2 t}{1 + q_e K_2 t} \quad (5)$$

where q_t ($\text{mg} \cdot \text{g}^{-1}$) is the As(V) sorption capacity at time t , k_1 (min^{-1}) and k_2 ($\text{g} \cdot \text{mg}^{-1} \text{ min}^{-1}$) are the equilibrium rate constant of pseudo first-order adsorption and pseudo second-order adsorption, respectively.

pH effect on As(V) removal by MgFe_2O_4 . To understand the influence of initial solution pH on the removal of As(V) by MgFe_2O_4 , the pH value of As(V) solutions was adjusted to 3–10. 0.5 g L^{-1} MgFe_2O_4 was added into 10 mg L^{-1} As(V) solutions with different initial pHs and treated for 5 h. The liquid was filtered using a $0.22 \mu\text{m}$ filter and the concentrations of As(V) in the solution was determined by ICP-MS.

Desorption and regeneration. To test the reusability of the as-prepared MgFe_2O_4 , the saturated adsorbent was desorbed under alkaline conditions and reused for As(V) adsorption for 6 consecutive cycles. In each cycle, 50 mg adsorbent was suspended in 100 mL As(V) solutions with a concentration of 10 mg L^{-1} for 5 h. Then, the adsorbent was separated magnetically and the As(V) loaded MgFe_2O_4 sample was regenerated by mixing with 50 mL of 1.0 mol L^{-1} NaOH solution for 12 h. Prior to the next adsorption-desorption cycle, the regenerated sorbent was washed thoroughly with deionized water till near neutral pH.

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