Combined effect of weak magnetic fields and anions on arsenite sequestration by zerovalent iron

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ABSTRACT: In this study, the effects of major anions (e.g., ClO_4^- , NO_3^- , Cl^- , and SO_4^{2-}) in water on the reactivity of zerovalent iron (ZVI) toward As(III) sequestration were evaluated with and without a weak magnetic field (WMF). Without WMF, ClO_4^- and NO_3^- had negligible influence on As(III) removal by ZVI but Cl^- and SO_4^{2-} could improve As(III) sequestration by ZVI. A synergetic effect of WMF and individual anion on improving As(III) removal by ZVI was observed for each of the investigated anion, which became more pronounced as the concentration of anion increased. The coupled influence of anions and WMF was associated with the simultaneous movement of anions with paramagnetic Fe^{2+} to keep local electroneutrality.

1 INTRODUCTION

There are many factors determining the reactivity of ZVI under realistic conditions, one of the most widely recognized and thoroughly studied being solution chemistry, especially the co-existing anions (Guan *et al.*, 2015; Sun *et al.*, 2016). In our recent studies, we have demonstrated that the application of a weak magnetic field (WMF) can accelerate the ZVI corrosion and thus enhance the removal of many toxic ions by ZVI. Taken together, the major anion effects on ZVI reactivity with the presence of a WMF may be quite different from that without WMF. However, this hypothesis has not been validated, to the best of our knowledge. So, the goals of this work are 1) to compare the effects of major anions on the kinetics of As(III) sequestration by ZVI with and without WMF; 2) investigate the potential mechanisms of coupled effects of anions and WMF on enhancing the ZVI reactivity.

2 METHODS/EXPERIMENTAL

2.1 Materials

All chemicals employed in this study were of analytical grade and used as received. The sodium salts of the anions were used. The iron particles were obtained from the Shanghai Jinshan reduced iron powder factory (China), which had a mean diameter of 40 μm and a BET surface area of 0.76 $\text{m}^2 \text{g}^{-1}$. All experiments were conducted using the ultrapure water (UP water) produced by a Milli-Q Reference water purification system.

2.2 Batch experiments

The experimental setup described in our previous study was also used in this study (Sun *et al.*, 2014). Briefly,

a permanent magnet with a diameter of 20 mm and thickness of 1 mm was placed under the reactor, which could provide a maximum magnetic field flux intensity of $\sim 15 \text{ mT}$ at the bottom of the reactor. The working solutions ($1000 \mu\text{g L}^{-1}$ As(III), Se(IV), Sb(V), or Cr(VI) solutions with different co-existing anions of different concentrations) were freshly prepared for each batch test. If it was not otherwise specified, the pH_{ini} value of the working solution was adjusted to 7.0 by dropwise addition of NaOH after the dosing of ClO_4^- , NO_3^- , Cl^- , SO_4^{2-} , and/or H_2PO_4^- to avoid introducing other anions.

3 RESULTS AND DISCUSSION

3.1 Effect of major anions on As(III) removal with and without WMF

Without WMF, ClO_4^- and NO_3^- had negligible influence on As(III) removal by ZVI but Cl^- and SO_4^{2-} could improve As(III) sequestration by ZVI. Moreover, the WMF-enhancing effect on As(III) removal by ZVI was minor in ultrapure water. A synergetic effect of WMF and individual anion on improving As(III) removal by ZVI was observed for each of the investigated anion, which became more pronounced as the concentration of anion increased, as shown in Figure 1.

Based on the extent of enhancing effects, these anions were ranked in the order of $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^- \approx \text{ClO}_4^-$ (from most to least enhanced). Compared to ClO_4^- and NO_3^- , Cl^- is believed to be much more aggressive towards passivating oxides because they diffuse readily into the film and form strong complexes with iron centers. These complexes can enhance the dissolution of iron oxide and often cause pitting corrosion. Accordingly, it was not unusual to

Figure 1. Rate constants of As(III) removal by ZVI with different anions in the absence or presence of WMF (ZVI = 0.20 g L⁻¹, As(III) = 1000 µg L⁻¹, T = 25°C). The annotating numbers represent the initial concentrations of corresponding anions (mM).

Figure 2. Proposed schematic illustration of the combined effects of WMF and anions on ZVI corrosion.

observe a better ZVI performance with Cl⁻ irrespective of the presence of WMF. Although many studies have reported that SO₄²⁻ could improve the ZVI performance, it was surprised to find that the performance with the presence of 0.01–1 mM SO₄²⁻ in the presence of WMF was much better than Cl⁻.

3.2 Role of co-existing anions on the reactivity of ZVI with WMF

Recently, it has been verified that magnetic field gradient force ($F_{\Delta B}$) was the major driving force for the WMF-induced improvement of ZVI reactivity. Being pulled by $F_{\Delta B}$, the paramagnetic Fe²⁺ generated in

ZVI corrosion tends to move along the magnetic lines to the place with higher magnetic field flux intensity, thereby resulting in an uneven distribution of Fe²⁺ and eventually localized distribution of oxide films on ZVI surface (Li *et al.*, 2017).

With regard to the role of anions, the principle of local electroneutrality should be emphasized. Given Fe²⁺ is positively charged, its movement will lead to an accumulation of positive charges in the high $|B_{\Delta B}|$ regions. Thus, for the anion-free cases, due to electrostatic exclusion, the accumulation of Fe²⁺ would suppress the further movement of Fe²⁺. However, for anion-containing scenario, since the co-existing anions can balance the positive charges, the transport of Fe²⁺ can be maintained and thereby the ZVI corrosion process can be sustained (Fig. 2).

4 CONCLUSIONS

These findings improved our understanding of the effects of anions on ZVI performance and thus could benefit the design and operation of a ZVI based technology. Another implication of this work should be a new method by taking advantage of the combined effect of WMF (or pre-magnetization) and anions (e.g., SO₄²⁻) can be developed either to enhance iron reactivity or to overcome the adverse effect of co-solutes. It should be noted that, the introduction of WMF/anions could enhance the ZVI reactivity towards many other oxyanions besides As(III), for example, Cr(VI) and Se(IV).

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Remediation of arsenic contaminated groundwater with magnetite (Fe₃O₄) and chitosan coated Fe₃O₄ nanoparticles

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ABSTRACT: Nanoparticles, due to their high surface area, regenerative properties and possibility of in situ treatment, exhibited their application potential in capturing arsenic (As). The objective of the current study is to explore the potential of As adsorption by Fe₃O₄ nanoparticles (IONPs) and Chitosan coated Fe₃O₄ nanoparticles (Ch-IONPs). Batch experiments performed with an initial As(III) and As(V) concentration of 0.125 mg L⁻¹, revealed a maximum As removal of 99.9% in 0.4 g L⁻¹ IONPs and 0.6 g L⁻¹ Ch-IONPs, at a pH equal to 7.0 and room temperature. The maximum adsorption capacity of IONPs and Ch-IONPs was 213.25 and 118.67 µg g⁻¹ for As(III) and 239.50 and 116.33 µg g⁻¹ for As(V), respectively. The Pearson Correlation value showed a better correlation with Freundlich isotherm (R² = 0.96) than Langmuir isotherm (R² = 0.87). The results of this work suggest that the incorporation of IONPs and Ch-IONPs as adsorbents, offer a promising option for As removal in water treatment.

1 INTRODUCTION

Arsenic (As) contamination in groundwater is a major global health concern. Arsenite [As(III)] is supposed to be 60 times more poisonous and mobile than arsenate [As(V)] (De *et al.*, 2009). Among various technologies already in use for removal of As from contaminated groundwater, namely coagulation, filtration, membrane separation and ion exchange; adsorption offers many advantages like ease of operation, simple waste handling and low operation cost. Magnetite (Fe₃O₄) nanoparticles exhibit excellent magnetic properties, which are being investigated for their application in water purification for the removal of heavy metals, such as lead and As (Feng *et al.*, 2012; Mayo *et al.*, 2007). The surface of these nanoparticles can be revamped according to desired functionalities, by methods like coating with surfactants or polymers. The aim of the current study is to find out the optimum conditions for the removal of As(III) and As(V) species by laboratory-synthesized Fe₃O₄ nanoparticles (IONPs) and chitosan coated Fe₃O₄ nanoparticles (Ch-IONPs). The removal capacity was studied by applying batch experiments and inferred by isotherm study.

2 MATERIALS AND METHODS

2.1 Synthesis of IONPs and Ch-IONPs

For the synthesis of IONPs by co-precipitation, 10 mg FeCl₃·6H₂O was dissolved in 200 mL distilled water. To this, 4 mg FeSO₄·7H₂O was added, and the mixture heated to 55°C for 10 min. NH₄OH was rapidly added to the heated mixture for maintaining pH at 10. The final solution was centrifuged, washed with distilled water and ethanol, finally oven dried for 12 hours. For the Ch-IONPs' synthesis, 5 mg FeCl₃·6H₂O

was mixed with 2 mg FeCl₂·4H₂O in 100 mL distilled water. Chitosan, 0.2 mg, was added in a 20 mL mixture of 1 mL acetic acid (2N) and 19 mL distilled water. Both the above mixtures were then mixed and pH was adjusted to 6.9. NH₄OH was then added after passing dry N₂ gas at 80°C. The final solution was centrifuged, washed with distilled water and ethanol, finally oven dried for 12 h.

2.2 Effect of pH and adsorbent dose on As(III) and As(V) removal

To study the effect of pH on As adsorption behavior of IONPs and Ch-IONPs, 50 mg of each of IONPs and Ch-IONPs were added in 50 mL NaAsO₂ solution (0.125 mg L⁻¹) and 50 mL NaHASO₄ solution (0.125 mg L⁻¹), respectively. Batch study for IONPs and Ch-IONPs was performed by adjusting the pH at 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0 in different batches (shaken for 60 minutes), adding 0.01 M HCl or 0.1 M NaOH. The study suggested an optimum pH of 7.0, which was kept constant and the dosage of IONPs and Ch-IONPs was varied, i.e. 5, 10, 15, 20, 30, 40 and 50 mg in each batch of 50 mL NaAsO₂ solution and 50 mL NaHASO₄ solution, respectively, to optimize the adsorbent dose for As(III) and As(V) adsorption and shaken for 60 min.

3 RESULTS AND DISCUSSION

3.1 Characterization of IONPs

The morphology of IONPs was studied using Field Emission Scanning Electron Microscope (FESEM), which confirms the formation of peanut shaped IONPs with an average size of 30 to 80 nm. The FESEM images of IONPs and Ch-IONPs are shown in