Remediation of arsenic(III) from aqueous solutions using zero-valent iron (ZVI) combined with potassium permanganate and ferrous ions

Wenna Deng, Zimai Zhou, Xuan Zhang, Yilin Yang, Yanqiu Sun, Yue Wang and Tingyi Liu

ABSTRACT

A system of zerovalent iron combined with potassium permanganate and ferrous irons (Fe(II)-KMnO4-ZVI) was used to remove As(III), one of the most poisonous wastewater pollutants. The Fe(II)-KMnO4-ZVI system was characterized by using X-ray photoelectron spectroscopy and scanning electron microscopy. The As(III) removal efficiency by the Fe(II)-KMnO4-ZVI system under different conditions was investigated and the experimental data were fitted to adsorption kinetics and isotherm models. As(III) could be removed by both physisorption and chemisorption through mixing adsorbents in a very short time (minute scale) with high removal ratios (more than 99.5%) over a wide range of pH (1–9) and concentration (20–100 mg/L). The removal of As(III) by the Fe(II)-KMnO4-ZVI system agreed well with pseudo-first-order reaction kinetics and pseudo-second-order reaction kinetics. The Freundlich isotherm provided a good model of the adsorption system, indicating that the Fe(II)-KMnO4-ZVI system has heterogeneous structure. The results show that the Fe(II)-KMnO4-ZVI system exhibited a high removal efficiency for As(III), which suggested that it might be an effective material for As(III) remediation.

INTRODUCTION

Due to the increasing population and industrial activities, the water contaminated by heavy metals (HMs) threatens our human health seriously. Arsenic, a semimetal, was found to pose serious adverse effects on human health through arsenic-contaminated drinking water. The World Health Organization revised the drinking water standard for arsenic from 50 to 10 μg/L in 2004. The traditional technologies for treatment of arsenic wastewater, including membrane filtration, ion exchange, adsorption and nano zero-valent iron (ZVI) (Fu & Wang 2014), have been extensively studied. However, because of the defects of these methods such as high operation costs and production of concentrated sludge, these technologies are not suitable for arsenic removal. Consequently, developing an alternative technique with environmental friendliness, simple operation and high removal efficiency for arsenic is urgently required.

For its low cost, non-toxicity, easy processing and availability, ZVI has been used broadly to remediate HMs from contaminated water in recent years. Also, ZVI has great potential in removing arsenic in situ and ex situ from groundwater and wastewater through various mechanisms including adsorption, precipitation, and co-precipitation. The main limitations of ZVI in treatment of arsenic wastewater are as follows: low reactivity because the oxide film forms quickly on ZVI after reaction, which limits the working efficiency, narrow working pH, and permeability decreased on account of precipitation of metal oxides and hydroxides.

Surveys conducted by Ghauch (2015) have shown that Fe0/H2O systems are operating in aqueous solutions through adsorption of contaminants after the formation of a porous nascent oxide. In order to optimize the decontaminating effect, it is a good idea to introduce some oxidizing agent into the Fe0/H2O system for oxidizing ZVI into ferric oxide and hydroxide effectively. Guo et al. (2016) reported that common oxidants (i.e., NaClO, KMnO4, H2O2) can continuously accelerate Fe0 corrosion, driving rapid and efficient removal of HMs by ZVI under the experimental conditions. Compared with sodium hypochlorite and hydrogen peroxide,
potassium permanganate has certain advantages. It does not produce harmful by-products, and it is easy to be applied and affordable. In addition to that, it is a ‘green’ strong oxidizer with high selectivity and activity, as well as superb ability for oxidation and coagulation. However, the most important feature of potassium hypermanganate is its reaction product, manganese dioxide, which is a hydrophilic colloid and could enable the potassium hypermanganate to have high removal efficiency for pollutants, especially HMs, in both acid and neutral reaction solution. Beyond that, Straub et al. (1996) reported a new practice that uses ferrous iron to make autotrophic denitrifier, in which ferrous iron acts as an electron donor. Since then the autotrophic denitrification has drawn wide attention due to its novelty and eco-friendliness. This new material is also promising to treat wastewaters, because firstly ferrous salt is much cheaper than alcohol or acetate, and secondly in situ formed ferric iron could serve as coagulants for HMs removal from wastewaters. Moreover, Lee et al. (2003) applied ferrous iron in an experiment in which As(III) was oxidized by oxygen and removed by Fe(III) coagulation. Inspired by these ideas, we tried to add iron ions in experiments and compared ferric iron ions with bivalent iron ions. The results showed that ammonium ferrous sulfate could further enhance the removal ratio.

To our knowledge, the removal of As(III) by the system in which ZVI is combined with potassium hypermanganate and ferrous ion has not been studied to date. Therefore, in this study, a system of Fe(II)-KMnO₄-ZVI was used to remove As(III) from wastewater. The main objectives are to: (1) characterize the Fe(II)-KMnO₄-ZVI system and its reaction products using spectroscope techniques, (2) investigate the effects of ZVI dosage and other chemistry factors (pH, temperature) on the As(III) adsorption, (3) demonstrate the role of Fe(II) and potassium hypermanganate in the system and discuss the detailed mechanisms by which KMnO₄ and Fe(II) remarkably enhanced the As(III) removal by ZVI. We hope that our findings may provide a new efficient adsorption material for removal of wastewater containing arsenic.

**EXPERIMENTAL METHODS**

**Chemicals**

Reduced iron powder (ZVI) and potassium hypermanganate (KMnO₄) were purchased from Fuchen Chemical Reagent Manufactory (Tianjin, China), and the iron content of powder was more than 98%. Ammonium ferrous sulfate ((NH₄)₂Fe(SO₄)₂·6H₂O) was purchased from Xingai Technology Development Co., Ltd (Tianjin, China). NaAsO₂ solution (1 g/L) was provided by National Centre for Certified Reference Materials (Beijing, China). All glassware and sample vessels used for the experiments and analysis were soaked in 15% HCl solution, flushed with tap water and rinsed at least three times with deionized water before use. All other chemicals were of analytical grade purity.

**Batch As(III) removal experiments**

Effects of different experimental conditions on the removal efficiency and kinetics of As(III) were studied using batch experiment as the following procedures. The pH values of individual samples were adjusted with dilute HNO₃ and/or NaOH solution to designated values in the range of 1–9 during the agitating process with a glass rod. Initial arsenic concentration varied from 20 mg/L to 100 mg/L. In each test, 100 mL of solution containing different amounts of arsenic was added to the vessel, which contained certain weight of ZVI, KMnO₄, and Fe(II) at set temperature, and mechanically agitated using a water-bathing constant temperature vibrator (XMTB) (160 r/min) for a total of 1 h. Then, the mixing solution was withdrawn at 0.5 min, 1 min, 2 min, 5 min, 10 min, 20 min, 30 min and 1 h respectively using a 10 mL disposable syringe and filtered through a 0.22 μm filter before the chemical analysis. The specific parameters of our batch exploring experiments can be seen in Table 1. The arsenic concentrations were measured by an inductively coupled plasma optical emission spectrometer (ICP-OES, Perkin Elmer Optima, USA). Arsenic removal by ZVI in the absence of oxidant was performed as a control. All batch experiments were conducted in duplicate.

**Analytical procedures**

The effect of pH value, adsorbent dosages and the reaction temperature on the reduction kinetics of As(III) was studied in accordance with previously reported procedures (Li et al. 2014). The Langmuir and Freundlich adsorption isotherm parameters were employed to evaluate the feasibility and nature of the adsorption process (Iftikhar et al. 2009).

The effluent was then directly diluted to the appropriate concentration for As analysis by an ICP-OES (Perkin Elmer Optima, USA). The X-ray diffraction (XRD) pattern of the Fe(II)-KMnO₄-ZVI system was performed on an X-ray diffractometer (X’Pert PRO, PANalytical, The Netherlands) equipped with a copper target at 40 KV and 40 mA. The
micro-morphological images of the Fe(II)-KMnO$_4$-ZVI system before and after use were observed by a field-emission scanning electron microscope (SEM) with an energy dispersive spectrometer (S-4800, Hitachi, Japan) at an accelerating voltage of 10–20 kV. The Fe(II)-KMnO$_4$-ZVI system particles collected after the batch experiments were vacuum-freeze dried before X-ray photoelectron spectroscopy (XPS) analysis (ESCLALAB 250Xi; Thermo Fisher, UK). For wide scan spectra, the energy spectrum ranges from 0 to 1,350 eV. The XPS results were collected in binding energy forms and fitted using the software Origin 8.6. The removal capacity, $q_e$, of the Fe(II)-KMnO$_4$-ZVI system for the arsenic ions was calculated according to the following equation:

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

where $C_0$ is the initial arsenic concentration in the solution (mg/L), $C_e$ is the equilibrium concentration of arsenic ions after reaction with the Fe(II)-KMnO$_4$-ZVI system (mg/L), $V$ is the arsenic solution volume (L) and $m$ is the mass of ZVI (g).

### RESULTS AND DISCUSSION

#### Adsorbents characterization

The morphology characterization of ZVI and the other two mixing adsorbents is shown in Figure 1. It can be seen that the SEM image of ZVI particles (0.5 g) in decontaminated arsenic wastewater (100 mL, 20 mg/L) in the absence of the other two adsorbents aggregated together, showing a dense and compact structure (from Figure 1(a)), while there is no visible attachment point and the range of particle diameters is about 6 μm, reflecting low extent of surface corrosion. However, when potassium permanganate (0.1 g) was added into the system, there is no concrete and complete block but some small flocs adhered to the surface (from Figure 1(b)). When the three adsorbents (ZVI: 0.5 g, KMnO$_4$: 0.01 g, Fe$^{2+}$: 0.02 g) were put into the system together to decontaminate arsenic (100 mL, 20 mg/L) from wastewater, the surface morphology of Fe(II)-KMnO$_4$-ZVI became very irregular and rugged in the range of 1–10 μm (from Figure 1(d)) after decontamination of the wastewater. In addition note that the scale bar of Figure 1(c) is 1 mm, while the scale bar of Figure 1(d) is 500 nm, so the particle became smaller as well as the specific surface areas, and system dispersion increased a lot after Fe(II) was added. According to Guo et al. (2018), the intensive surface reaction between ZVI, ferrous ammonium sulfate, and potassium permanganate may produce a large amount of iron oxyhydroxides, such as magnetite oxides, and various amorphous phases of iron oxides/hydroxides, indicating more activated sites among the surface of the complex were produced.

#### Kinetics of As(III) removal by Fe(II)-KMnO$_4$-ZVI system

The pH of solution has been considered as the most important variable affecting metal adsorption onto adsorbent. This is partly because the solution pH affects the surface charges of adsorbents and the speciation of metal ions, and hence the interactions between metal ions and adsorbent surfaces (Doula 2009). The effects of pH (1–9) on the adsorption of arsenic by the Fe(II)-KMnO$_4$-ZVI system (20–100 mg/L) were studied (Figure 2(a) and insert). It is evident that the removal ratio decreased with the increase of initial pH and the removal ratios were all more than 99.5% after 30 min in the pH range of 1–7. However, it could be seen from the charts that the removal ratio is relatively lower than others when solution pH is around 9. This phenomenon may be associated with the variation of arsenate species and the surface charge of ferric/ferrous hydroxide with pH. According to the previous literature (Liu et al. 2013a, 2013b), at pH 6.0, As(III) species are present totally in ionic state. Since ~99.95% As(III) was adsorbed at pH 6.0, it may safely be stated that the removal of As(III) was mostly due to adsorption and not precipitation. At pH > 7.0, As(III) would begin to form precipitation if no As(III)

### Table 1 | Control variable of batch tests

<table>
<thead>
<tr>
<th>Batch experiments</th>
<th>The value of pH</th>
<th>Initial concentration of As(III) (mg/L)</th>
<th>Reaction temperature (°C)</th>
<th>The dosage of ZVI (g)</th>
<th>The dosage of KMnO$_4$ (g)</th>
<th>The dosage of Fe$_{2+}$ (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,2,3,5,7,9</td>
<td>20</td>
<td>20</td>
<td>0.5</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>2</td>
<td>7</td>
<td>20,40,80,100</td>
<td>20</td>
<td>0.5</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>20</td>
<td>20,25,30,35</td>
<td>0.5</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>20</td>
<td>20</td>
<td>0.02,0.1,0.5</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>
is adsorbed on the Fe(II)-KMnO₄-ZVI system. The phenomenon may be explained by ZVI corrosion rates. The pH of the solution is inversely proportional to the corrosion rate of ZVI. With the increase of the solution pH, the percentage of ZVI getting corroded decreased sharply. The corrosion situation is likely to be positively related to the adsorption. In combination with the idea that Fe oxide or hydroxyl species could greatly improve the removal of HMs from water, this explains why HMs removal percentage decreased with the increase of solution pH. A similar trend for As(III) removal has been observed using goethite (Dogán et al. 2010). This phenomenon may also be explained by competitive adsorption sites. When in alkaline conditions, the concentration of hydroxyl ions in the solution increases and the ions will compete for active sites with arsenic acid radical anion, thus leading to relatively lower removal ratio. Chwirka et al. (2000) have shown that the pH value of aqueous solution is greatly influential for arsenic removal with iron oxide. When the iron salts such as ferric trichloride entered the water, they would form hydrolyzed iron hydroxide, whose surface consists of many positively charged particles. Arsenate is easily adsorbed onto the positively charged hydrogen ferric oxide particles for it is an anion. When the solution pH value increased, the positive charge on the surface of the iron hydroxide would be reduced, reducing the arsenic removal ratio.

This research adopts the pseudo-first-order kinetics model and the pseudo-second-order kinetics model for fitting experimental data. The pseudo-first-order kinetics and pseudo-second-order expression are defined as follows.
respectively (Alowitz & Scherer 2002):

\[ V = \frac{d[C]}{dt} = K_{obs} \]  

\[ t = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \]  

where \( V \) is the first order reaction rate, \( K_{obs} \) is the first-order reaction performance rate constant for the decontamination reaction of arsenic, \( k_2 \) is the pseudo-second-order rate constant \((g/(mg\cdot min))\), \( q_e \) is the amount of As(III) adsorbed at equilibrium condition \((mg/g)\), and \( q_t \) is the amount of As(III) on the surface of adsorbents in reaction at any time \( t \) \((mg/g)\).

It can be seen from Figure 2(a) that \( K_{obs} \) of As(III) removal displayed a good linearity with pH values with correlation coefficient \( R^2 \) more than 0.9998. The figure inserted shows the effect of pH on removal of arsenic and indicates that the removal ratio of As(III) by the Fe(II)-KMnO\(_4\)-ZVI system agreed well with the pseudo-first-order reaction kinetics. The similar phenomenon had also been found in other systems using nanoscale iron supported on chitosan and pumice beads (Liu et al. 2012, 2015). Furthermore, it can be seen from Figure 2(b) that \( R^2 \) is more than 0.998, indicating that there is strong positive correlation that As(III) absorption on the Fe(II)-KMnO\(_4\)-ZVI system follows the pseudo-second-order kinetic expression. The pseudo second order dynamics model assumes that the adsorption process involves two reaction steps which include electrostatic adherence and surface complexion (Wy et al. 2014), and the two phases can take place simultaneously; the rate of the first reaction step is very rapid, so the first phase is short, while the duration of the second stage is longer. However, those trend lines were nearly identical at different pH values, which means that the nature of adsorption of arsenic on the Fe(II)-KMnO\(_4\)-ZVI system was almost the same at wide pH ranges.

**Effect of initial concentration on adsorption effect**

Experiments were performed to determine the effect of initial concentration of arsenic on the adsorption capacity of the Fe(II)-KMnO\(_4\)-ZVI system. From Figure 3(a), it could be found that the removal percentage reached 99.57%, 99.06%, 98.02%, and 98.02% at 20, 40, 80 and 100 mg/L arsenic, respectively, indicating that the arsenic removal ratio decreased a bit with the increase of initial solution concentration. Figure 3(b) shows the comparison of final equilibrium concentrations with the integrated sewage discharge standards of GB 8978–1996. According to the integrated wastewater discharge standard regulations, the allowable emission concentration of total arsenic is 0.5 mg/L. In the graph, we compared the remaining arsenic concentration with the largest permitted discharge concentration. If the ratio of standard discharge concentration is greater than 50%, the processing results meet the discharge standard. If the rate is higher, the removal capacity is much more efficient too. With the increase of initial concentration, it can be seen clearly from the diagram that the removal ratio declined. However, the minimum removal percentage has also reached the integrated wastewater discharge standard. The higher adsorption capacity for arsenic in this study may be due to the complex cooperation between ZVI, ammonium ferrous sulfate and potassium permanganate. From the result of the experiment, it can be interpreted that the higher removal percentage with low initial solution concentration may be due to the sufficient active reaction sites. With the increase of initial solution concentration, the active reaction sites became insufficient, and then the removal capacity began to decline.
As(III) adsorption isotherms

An adsorption isotherm describes an adsorption equilibrium condition of a certain substance on the interface of two materials at set temperature. Adsorption isotherms can explain the relationship between adsorbate and adsorbent and provide the parameter for designing a desired adsorption method. Isotherms that are commonly used are Langmuir isotherm and Freundlich model (Chen 2015).

The Langmuir isotherm model can be represented as follows:

\[
\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{k_L q_m}
\]

(4)

where \( C_e \) (mg/L) is the adsorption equilibrium concentration, \( q_e \) (mg/g) is the adsorption capacity in equilibrium state, \( q_m \) (mg/g) is the maximum adsorbing capacity, \( k_L \) (L/mg) is the adsorption equilibrium constant of Langmuir. Also a dimensionless dissociation constant \( R_L \) can be defined according to the Langmuir model.

\[
R_L = \frac{1}{1 + k_L C_0}
\]

(5)

where \( k_L \) (L/mg) is the Langmuir constant, and \( C_0 \) (mg/L) is the highest initial concentration of adsorbents. According to the value of \( R_L \), the adsorption process can be divided into four categories: preferential adsorption (\( R_L > 1 \)),
linear adsorption ($R_L = 1$), favorable adsorption ($0 < R_L < 1$) and irreversible adsorption ($R_L = 0$).

The Freundlich isotherm model can be represented as follows:

$$\ln q_e = \frac{1}{n} \ln C_e + \ln k_F$$  

(6)

where $k_F$ (mg/L) is the adsorption equilibrium constant; $1/n$ represents the dimensionless constant of adsorption. It is generally believed that the reaction is easier when $0.1 < 1/n < 1$, while it becomes more difficult when $1/n > 1$.

Adsorption equilibrium data are usually shown in the form of an isotherm model, reflecting the variation of adsorption capacity with different adsorption temperature (Su et al. 2014). It is indispensable to establish the suitable adsorption models in order to better understand the adsorption behavior and mechanism. The relative parameters calculated from the two models are listed in Table S1, Supplementary Information (available with the online version of this paper). The higher correlation coefficient ($R^2 = 0.9703–0.9857$) of the Freundlich model indicates that the adsorption data are better fitted by the Freundlich model than the Langmuir model ($R^2 = 0.892–0.932$). As we know, the Langmuir model assumes that adsorption is monolayer on uniform sites of a homogeneous surface without interaction between any adsorbate and molecules, while the Freundlich model is based on other assumptions that each adsorption site can interact with only adsorbate molecules, and the heterogeneous adsorbent surface possesses a certain number of adsorption sites. The adsorption heat of arsenic may decrease linearly with the coverage of adsorption sites and the adsorbent surface was closely homogeneous for arsenic (Guo et al. 2015). This means that the adsorption capacity is in accordance with the adsorption temperature. However, it was difficult to distinguish the determinant of surface heterogeneity or homogeneity; this might depend on the interaction and adsorption energy between adsorbents and adsorbates.

**The removal mechanism of As(III)**

The results of XPS characterization of the Fe(II)-KMnO₄-ZVI system before and after As(III) adsorption are shown in Figure 4. A new peak at the binding energy of 44 eV appeared after As(III) adsorption (Figure 4, plot (b)), which is assigned to the phenomenon peak of As, and this indicates that As was absorbed by the Fe(II)-KMnO₄-ZVI system after reaction. The results of Table 2 show that before As(III) adsorption, the mass ratio of O, Mn, Fe and As was 46.57%, 2.68%, 7.48% and 0.42%, respectively. This phenomenon indicated the uptake of As on the surface of the Fe(II)-KMnO₄-ZVI system.

Detailed XPS surveys on the region of As3d at different reaction moments are shown in Figure 5. The photoelectron peak for As concentrated at 47.8 eV and 47.6 eV, which corresponded to As(V). This result showed that As(III) was oxidized quickly by potassium permanganate into As(V).

In addition, ZVI, KMnO₄-ZVI, Fe(III)-KMnO₄-ZVI and Fe(II)-KMnO₄-ZVI systems were respectively used as adsorbents to remove As(III) from contaminated water and the results showed that the Fe(II)-KMnO₄-ZVI system could highly remove As(III) from water. As shown in Figure 6, the adsorption efficiency of arsenic on adsorbents was in the order of Fe(II)-KMnO₄-ZVI > Fe(III)-KMnO₄-ZVI > KMnO₄-ZVI > ZVI. Obviously, during the experiment, the Fe(II) and KMnO₄ fraction played important roles in the adsorption process of arsenic on ZVI. Using only ZVI results in low arsenic decontamination efficiency (<10%).

According to Guo et al. (2015), using only ZVI to remove As(III) from contaminated water is an electrochemical process.

| Table 2 | The mass ratio of element on Fe(II)-KMnO₄-ZVI system before and after As(III) adsorption |
|---------|---------------------|----------------|----------------|----------------|
| The mass ratio (%) | O1s | Mn2p3 | Fe2p3 | As3d |
| Before | 30.07 | 0.88 | 4.29 | 0.00 |
| After | 46.59 | 2.68 | 7.48 | 0.42 |
which includes the iron dissolution coupled with electron consumption, and the adsorption efficiency is proportional to the corrosion rate of ZVI. In addition to that, according to a previous study (Guan et al. 2013), a thin passive layer of Fe oxide or hydroxyl species would be formed soon after and protect low iron from corrosion, for those passive species are insoluble in non-acidic solution. In recent years, there has been an increasing amount of literature concluding that besides ZVI itself, the complex species of ferric/ferrous oxides and oxyhydroxides coated on the ZVI surface are important reactive components responsible for HMs removal via various mechanisms, such as adsorption, precipitation, co-precipitation, and size-exclusion (Puls et al. 1999). So on the one hand, the reasons for the relatively low removal capacity of ZVI are derived from limited content of oxidant in water and numbered corrosion products could explain the partial removal of As(III). On the other hand, this passive layer formed on the sphere of ZVI showed negative effect on further ZVI
corrosion because it impedes the oxygen diffusion through these oxide barriers (Liang et al. 2014).

In contrast with the slow kinetics and inefficient removal of contaminants by ZVI alone, the coupling of common oxides with ZVI resulted in a comparatively rapid and high removal ratio (~30%) of As(III). A reasonable explanation is that KMnO₄ can react with ZVI surface at high rate and stability, driving very rapid and intensive iron corrosion, and concomitantly resulting in the continuous production of iron oxide and oxyhydroxides. Beyond that, potassium permanganate can also induce the oxidation of both As(III) and Fe(II). Fe(III) derived from Fe(II) (formed in situ) worked as the coagulant to remove arsenic in the process. The oxidants (1 mM) added into the ZVI system can be completely consumed within 10 min, indicating that they can quickly attack and oxidize the ZVI surface. As is indicated in Figure 1(a), the SEM image of ZVI in the absence of oxidants showed a dense and compact structure, reflecting low extent of surface corrosion. However, when the oxidant was dosed, the surface of the used ZVI became very irregular and rugged after column running, indicating an intensive corrosion process had been occurring (Figure 1(b)). The intensive surface reaction between ZVI, potassium permanganate and ferrous iron produced a large amount of oxyhydroxides. These iron oxides were exhibited as micro- or nano-sized colloids in the SEM images (Figure 1(b)) suggesting a large specific surface area on the activated ZVI surface. They play a critical role in As(III) removal through multiple mechanisms including adsorption, precipitation, and co-precipitation.

In the Fe(II)-KMnO₄-ZVI system, As(III) was oxidized by KMnO₄ and then removed by Fe(III) coagulation. However, As(III) was oxidized by KMnO₄ and then removed by the Fe(III) formed in situ in the Fe(II)-KMnO₄-ZVI process. The great difference may be ascribed to different properties of conventional Fe(III) and the Fe(III) formed in situ and the different amounts of MnO₂ formed in situ. According to the studies of Guan et al. (2009), the uptake of As(V) by MnO₂ formed in situ was examined and the results showed that only 1.4–3.2% and 2.0–5.6% of arsenate was removed by 10 μM and 18.6 μM MnO₂ formed in situ, respectively. Therefore, the great difference in arsenic removal in these two systems (Fe(II)-KMnO₄-ZVI system and Fe(III)-KMnO₄-ZVI system) was not ascribed to the uptake of arsenic by the MnO₂ formed in situ but to the different properties of conventional Fe(III) and the Fe(III) formed in situ. It is possible that Fe(III) formed in situ is more effective than the conventional Fe(III) salts in removing other contaminants, such as phosphate, natural organic matter and so on.

As indicated in Figure 2(a), we can see clearly that the removal percentage decreased with an increase of the initial pH, which may be partly because the released H⁺ iron in acid solution accelerated remarkably the iron corrosion rate, which could facilitate the Fenton-like reaction in the presence of oxidants (Wang et al. 2010), and promote the oxidation of As(III) and Fe(II), as follows:

$$\text{Fe}^0 + 2\text{H}^+ + \text{O}_2 = \text{Fe}^{2+} + \text{H}_2\text{O}_2$$  \hspace{1cm} (7)

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 = \text{Fe}^{3+} + 2\text{HO}$$  \hspace{1cm} (8)

It is well known that the oxidation potential and the reduction products of potassium permanganate are pH-dominated. Under acidic conditions the oxidation half-reaction is (Weast et al. 1988):

$$\text{MnO}_4^- + 8\text{H}^+ + 5e = \text{Mn}^{2+} + 4\text{H}_2\text{O} \quad E^0 = +1.51 \text{V}$$  \hspace{1cm} (9)

Under weak acidic, neutral and weak alkaline conditions, the half-reaction is:

$$\text{MnO}_4^- + 2\text{H}_2\text{O} + 5e = \text{MnO}_2(s) + 4\text{OH}^- \quad E^0 = +0.588 \text{V}$$  \hspace{1cm} (10)

Therefore the oxidation reactions of As(III) and Fe(II) by permanganate are possibly as follows:

$$5\text{H}_3\text{AsO}_3 + 2\text{MnO}_4^- = 5\text{AsO}_4^{3-} + 2\text{Mn}^{2+} + 3\text{H}_2\text{O} + 9\text{H}^+$$  \hspace{1cm} (11)

$$5\text{H}_3\text{AsO}_3 + 2\text{MnO}_4^- + 7\text{OH}^- = 5\text{AsO}_4^{3-} + 2\text{MnO}_2 + 8\text{H}_2\text{O}$$  \hspace{1cm} (12)

$$5\text{Fe}^{2+} + \text{MnO}_4^- + 11\text{H}_2\text{O} = 5\text{Fe(OH)}_3(s) + \text{Mn}^{2+} + 7\text{H}^+$$  \hspace{1cm} (13)

$$3\text{Fe}^{2+} + \text{MnO}_4^- + 5\text{H}_2\text{O} = 3\text{Fe(OH)}_3(s) + \text{MnO}_2 + \text{H}^+$$  \hspace{1cm} (14)

According to the studies of Jing et al. (2005), there seems to be an electron affinity between As and Fe, which formed As-Fe bond and then coagulated. Therefore, the interaction of arsenate with Fe(III) formed in situ was proposed, as illustrated in Figure 7.

Due to the high linear correlation with the pseudo-first-order as well as the pseudo-second-order reaction kinetics which we discussed earlier, it can be demonstrated that both physisorption and chemisorption played important roles in the adsorption process. This point could also be affirmed indirectly from Figure S1, Supplementary Information (available with the online version of this paper), which we took in the process of our experiment. The samples 1, 2, 3, 4, 5, 6, 7, and 8 are taken after reaction time of 0.5, 1, 2, 5, 10, 20, 30, and 60 minutes, respectively. The obvious color
change may be helpful for elucidating the reaction process. The first three samples look pale red, and the next two samples appear orange-yellow, while the next three samples are almost colorless. We can infer from this phenomenon that in the first 2 minutes of the reaction, oxidation may be the main reaction in the system, while As(III) and Fe(II) were oxidized by KMnO₄ into As(V) and Fe(III). The reaction went on, and the sample color indicated that the co-precipitation and coagulation reactions play a dominant role in the process. After that, the reaction came into a state of equilibrium, and the removal percentage went up to 92.5%. Then the reaction processed slowly, and at the end, the removal percentage came to 99.93%, reaching drinking water standards.

In the experiment, it was found that the old layers of the products fell off the ZVI surface as detached colloids, although the newly formed iron oxides and hydroxides which derived from the coupled oxidants were coated on the ZVI surface. Very similar to the particulate matter removal by rapid filtration using granular sands, these iron minerals as generated were sequestered and permanently stayed in the reaction system, still bearing the capacity for binding HMs. In the whole reaction process, it was found that the oxidants were soon consumed by the packed ZVI, and the concentration of oxidants from effluent became ignorable, which indicated that four processes had been occurring during the column running. These four processes were the rapid iron corrosion driving by the oxidant dosing, the continuous oxidation of As(III) and Fe(II), the continuous generation of reactive iron oxides sequestering in the gradual ZVI column, and the adsorption, co-precipitation and coagulation removal of As(V). During the column running, the newly formed and fresh iron oxides and hydroxides could continuously compensate for the old and saturated components of them for the further As(III) removal. This steady surface corrosion and arsenic removal enabled the combined system to remove As(III) with high efficiency and per durability. Alternatively in the mixing method, those detached colloids loaded with arsenic may be further clarified with centrifugation, granular or membrane filtration.

Figure 7 | Possible complexation reactions of As(V) with Fe(III) formed in situ (As(III) = 20 mg/L, KMnO₄ = 6.2 μM, Fe(II) = 2.5 μM).

Figure 8 | Schematic model of fast and efficient removal of As(III) by Fe(II)-KMnO₄-ZVI system.
From the mechanisms we discussed above, we can briefly represent our results in Figure 8 in a schematic model. In summary, the results of this study showed that the Fe(II)-KMnO₄-ZVI system was an efficient material for the treatment of HMs and might be used as an effective material for permeable reactive barriers as well as ex situ remediation.

CONCLUSIONS

In this study, the system of ZVI combined with potassium permanganate and ferrous ions was developed to remove As(III) from synthetic wastewater. Effects of parameters including ZVI dosage, initial concentration and the solution pH on the As(III) removal were investigated. The physical characterization showed that the Fe(II)-KMnO₄-ZVI system had a high surface area and negatively charged surface, facilitating its application for absorbing metal cations such as arsenic from water. The adsorption isotherms and kinetics were employed to investigate the adsorption behavior. Compared with the Langmuir model, the Freundlich model showed a strong linear dependence, which means that the adsorption capacity is in accordance with the adsorption temperature. Pseudo-second-order model (R² > 0.99) was better fitted to the kinetic data than the pseudo-first-order model. The adsorption process was chemical adsorption mainly by ion exchange and complexation. The system can meet the demands for rapid and stable As(III) removal and showed wide application prospects in the removal of metal cations like arsenic from contaminated water.

ACKNOWLEDGEMENTS

The authors want to thank Zhigang Zhang, Qian Wang and Yuntao Shang for their support with analyses. This work was financially supported by the National Natural Science Foundation of China (21307090) and Tianjin Municipal Natural Science Foundation of China (14JCZDJC41000).

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First received 5 June 2017; accepted in revised form 19 September 2017. Available online 30 October 2017.