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Graphical abstract

**Effect of Pyrite on Enhancement of Zero-valent iron Corrosion
for Arsenic Removal in Water: A mechanistic study**

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Abstract: In this study, the enhanced effect of pyrite (FeS_2) on zero-valent iron (Fe^0) corrosion for arsenic (As) removal was investigated in a combined- Fe^0/FeS_2 system. The effects of different Fe^0/FeS_2 composition, dosage and initial pH were evaluated by batch experiments. Results showed that the best combination ratio of $\text{Fe}^0:\text{FeS}_2$ (w/w) was 1:1 and the optimal dosage of mixture was 2.0 g/L. The combination of Fe^0 and FeS_2 in a system significantly enhanced the reactivity of Fe^0 for effective As removal within a broad pH range (3.0~9.0). The effective As removal in the combined- Fe^0/FeS_2 system was primarily ascribed to being enhanced corrosion of Fe^0 by addition of FeS_2 . SEM and XRD characterizations strongly verified this point. Specifically, the mechanism study (the releases of Fe^{2+} and total Fe ion, variations of pH values as well as XPS characterization) suggested that FeS_2 in the combined- Fe^0/FeS_2 system could alleviate the passivation of Fe^0 (pH_{ini} 3.0~5.0) and accelerate the dissolution of pristine oxide film that coated on Fe^0 surface (pH_{ini} 6.8~9.0). Besides, FeS_2 in combined- Fe^0/FeS_2 system could also accelerate the reactions between Fe^0 to O_2 at pH_{ini} 3.0~9.0. These phenomena were well explained by a galvanic couple between Fe^0 and FeS_2 , where FeS_2 was a cathode and Fe^0 was an anode. Consequently, electrons released from Fe^0 that mediated by FeS_2 to oxide film, passivation layer and O_2 were accelerated in combined- Fe^0/FeS_2 system and thereby enhanced the corrosion of Fe^0 for efficient As removal. Our findings suggest that utilizing FeS_2 to enhance the corrosion of Fe^0 would be a promising technology for remediation of As-contaminated water.

Keywords: Zero-valent iron; Pyrite; enhanced corrosion; Arsenic removal

1 Introduction

Arsenic (As) is a typical toxic metalloid and it is widely distributed throughout the Earth's crust (Garelick et al., 2008). However, studies reported that increasing concentrations of As have been found in groundwater in many regions in recent years (Wai et al., 2012). Countries such as Bangladesh (Iaea, 2012), Vietnam (Christen, 2001), China (Zhang et al., 2016), Chile and south-western USA (Smedley and Kinniburgh, 2002) were all exposed to high levels of As-contaminated groundwater, where the concentration of As all exceeded WHO guideline values ($10 \mu\text{g L}^{-1}$). Therefore, the As contamination of groundwater is now a significant global problem (Clancy et al., 2013).

Several methods, such as co-precipitation, adsorption, ion exchange, membrane processes and electrocoagulation are always used to purify As-contaminated water (Bissen and Frimmel, 2003). Therein, zero-valent iron (Fe^0)-based adsorption technology has received much attention due to being cost-effective and environmental friendly for As removal (Sun et al., 2014). Previous studies indicated that in $\text{Fe}^0/\text{H}_2\text{O}/\text{O}_2$ system, As could be effectively removed through adsorption, precipitation and co-precipitation on/with iron corrosion products (Lackovic et al., 2000; Kanel et al., 2005; Leupin and Hug, 2005). Although Fe^0 exhibits good performance in As removal, there are still some existing challenges at present. The reactivity of Fe^0 is always deteriorated by its pristine oxide film, authigenic passivation (it was formed when Fe^0 contacted with water and contaminants) as well as high pH (Guan et al., 2015; Liang et al., 2013; Li et al., 2016). These factors can inhibit electron transfer

between Fe^0 and electron acceptors (O_2 , H^+ , contaminants) and thereby affect the corrosion performance of Fe^0 . Ultimately, they will give rise to an in-effective removal of contaminants (Sun et al., 2014; Dong et al., 2010). Therefore, numerous countermeasures have been developed to improve the corrosion of Fe^0 to enhance its reactivity. Measures includes the establishment of ultrasound/ Fe^0 compound systems (Geiger et al., 2002) and weak magnetic field (WMF)/ Fe^0 compound systems (Xu et al., 2016), application of nano-zero valent iron, Fe^0 -based bimetals (Ramos et al., 2009, Yan et al., 2010) and sulfide-modified zero-valent iron (Li et al., 2017). Among all of these, sulfidation treatment of Fe^0 has gained more preference due to its high reactivity. Sulfide-modified Fe^0 is generally characterized as a type of core-shell structure with a Fe^0 core and a FeS shell, sometimes including FeS_2 as well (Fan et al., 2017; Rajajayavel and Ghoshal, 2015). As a semiconductor, FeS is more conductive than pristine oxide film coated on Fe^0 and which can effectively promote corrosion of Fe^0 (Huang et al., 2018). Though sulfidation of Fe^0 could enhance the reactivity of Fe^0 , the introduction of sulfur-containing chemicals led to higher cost of environmental remediation technology based on Fe^0 . Hence, sulfidation of Fe^0 seems to be a cost measure to improve the reactivity of Fe^0 . Moreover, the procedures of sulfidation of Fe^0 were also complicated. Consequently, it is urgent at present to look for a more cost-effective, simple and environmentally friendly method to enhance the corrosion performance of Fe^0 .

Considering that pyrite (FeS_2) is a typical transition metal semiconductor that is the same to the FeS . So we proposed that the application of FeS_2 to improve the Fe^0

corrosion behavior and therefore to enhance the As removal efficiency. On one hand, FeS₂ has a narrow band gap of about 0.90eV and both n- and p- type conduction behaviors have been observed in natural crystals (Chernyshova, 2004; Schlegel and Wachter, 1976). This means that FeS₂ can act as a good mediator for electron transfer. Additionally, FeS₂ possesses a high reduction potential of about + 0.35 V. Hence, it always forms galvanic couple with other low-potential materials, and thereby promotes the corrosion of low-potential material (Lü et al., 2019; Ke et al., 2016). On the other hand, FeS₂ is not only an environmental remediation material that can sequester various environment pollutants (Sun et al., 2012; Zhang et al., 2015), but also a type of mineral waste residue which always causes serious Acid Mine Drainage (AMD) pollution (Pagnanelli et al., 2004). Therefore, utilizing FeS₂ to enhance the reactivity of Fe⁰ by simple mixing would be a more cost-effective, simple and environmentally friendly (reuse of waste) method for As removal. Previous studies showed that mixing FeS₂ and Fe⁰ together could be contributed to the high removal of Cr(VI) in column experiments (Lü et al., 2018). Min et al (2017) had prepared Fe⁰-FeS₂ adsorbent by facile ball milling to remove As from water. Results showed that the Fe⁰-FeS₂ adsorbent exhibited an excellent removal ability for As(III). However, with respect to the study of using FeS₂ and Fe⁰ by simple mixing to remove As from water has not been reported, and neither feasibility nor mechanism of As removal is yet clear. Hence, we conducted a series of batch experiments to explore these issues.

Accordingly, the main objectives of this work were to (1) investigate the

feasibility of utilizing FeS_2 to enhance the corrosion of Fe^0 for removing As from water; (2) evaluate the effects of different compositions of Fe^0/FeS_2 , dosage, and pH on As removal; (3) explore the mechanism of enhanced effect of FeS_2 on Fe^0 corrosion in the combined- Fe^0/FeS_2 .

2 Materials and Methods

2.1 Chemicals and Materials

All chemicals used in this study were analytical grade. Sodium arsenite (NaAsO_2 , 95%) was purchased from Xiya Reagent Factory, sodium arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, 98%) was purchased from Sigma-Aldrich, and potassium iodate (KIO_3 , 99.8%), ammonium iron (II) sulfate hexahydrate ($(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, 99.5%), hydroxylammonium chloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$, 98.5%) and 1,10-Phenanthroline monohydrate ($\text{C}_{12}\text{H}_8\text{N}_2 \cdot \text{H}_2\text{O}$, 98%) were purchased from Aladdin. Other reagents, 5, 5-Dimethyl-1-pyrroline N-oxide (DMPO, $\text{C}_6\text{H}_{11}\text{NO}$, 98%), ammonium molybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, 99%), potassium antimonyl tartrate trihydrate ($\text{C}_8\text{H}_4\text{K}_2\text{O}_{12}\text{Sb}_2 \cdot 3\text{H}_2\text{O}$, 99.5%), ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$, 99.7%), sodium acetate anhydrous (CH_3COONa , 99%), acetic acid ($\text{C}_2\text{H}_4\text{O}_2$, 99.5%), sodium hydroxide (NaOH , 96%), sulfuric acid (H_2SO_4 , 98%) and hydrochloric acid (HCl , 36%-38%) were also involved in this study. All solutions were prepared using deionized distilled water that produced by a Millipore Milli-Q system (USA) and the stock solutions were stored in a refrigerator at 4°C .

Zero-valent iron (Fe^0) powder used in this experiment was purchased from Aladdin, while pyrite (FeS_2) was obtained from Hunan Yaogangxian Mining Co., Ltd,

China. The detailed information of Fe^0 and FeS_2 could be found in Supplementary Table S1 and Fig.S1.

2.2 Batch experiments

Batch As removal experiments were carried out in a 1000 mL reactor and stirred with a mechanical stirrer at 400 rpm. This stirring speed was enough to ensure both Fe^0 and FeS_2 could uniformly disperse in reaction solution. The reaction system was always open to the air to provide an aerobic reaction environment. Working solution ($[\text{As(III)}] = 2 \text{ mg L}^{-1}$) was freshly prepared by adding 1 mL As(III) stock solution ($[\text{As(III)}] = 1000 \text{ mg L}^{-1}$) into 499 mL deionized water for each batch test. The initial pH values were adjusted with sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4). When the working solution was firstly stirred for 2 minutes, 2 mL of the solution was sampled by a syringe to determine the initial As(III) concentrations. With regard to initiating the reaction, Fe^0 and FeS_2 were simultaneously added into the solution. Then at a regular time interval, 2 mL of the solution was taken from reactor by a syringe and filtered through 0.45 μm membrane for analysis. All these experiments were performed in duplicate.

2.3 Analytical Methods

The aqueous concentration of As were measured using a molybdate-based method by a UV-visible spectrophotometer (TU-1810) at 880 nm (Dhar et al., 2004). The As removal rate was calculated by Eq.1. The Fe^{2+} concentration with and without 1,10-phenanthroline addition were determined by the 1,10-phenanthroline colorimetric method using an UV-visible spectrophotometer at 510 nm (Gilcreas,

1998). The pH values were determined by a Shanghai Leici E-201-C pH meter. The concentration of SO_4^{2-} was detected by Ion Chromatography (Dionex, ICS 1000, AS 14 column). FeS_2 , Fe^0 and the mixture of FeS_2 and Fe^0 before and after reaction were characterized by SEM (scanning electron microscope, FEI Q25), which was equipped with a ETD detector and operated at an acceleration voltage of 5 kV. XRD (X-ray diffraction) characterization was detected with a Empyrean diffraction system. XPS (X-ray photoelectron spectroscopy, PHI X-tool) characterization was conducted with a radiation source of Al $\text{K}\alpha$.

$$\text{As removal rate} = 1 - C_t/C_0 \quad (1)$$

Where C_t was the As concentration in reaction solution at different time intervals and C_0 was the initial As concentration.

3 Results and discussion

3.1 Effects of different compositions of the Fe^0/FeS_2 (w/w) mixture

To investigate the effect of different compositions of Fe^0/FeS_2 (w/w) mixture on As removal efficiency, batch experiments were conducted with Fe^0/FeS_2 ratios (w/w) of 1:0, 1:9, 1:4, 1:1, 4:1, 9:1 and 0:1 under near-neutral aerobic conditions ($\text{pH}_{\text{ini}} = 6.8$).

Obviously, results showed that the single- Fe^0 system (1:0) and single- FeS_2 system (0:1) exhibited lower As removal rate than the combined- Fe^0/FeS_2 systems. There was only 5.0% of As removed from the single- FeS_2 system and 49.3% from the single- Fe^0 system (Fig.1b). However, 90.8% of As was removed from the combined- Fe^0/FeS_2 system with ratios of 1:1. It indicated that FeS_2 was an inert As

removal material while Fe^0 was an relatively reactive one. The combination of Fe^0 with FeS_2 in a system could significantly enhance the As removal rate. The reason of the enhancement probably could be ascribed to the improved surface corrosion of Fe^0 by introducing FeS_2 , because surface corrosion is a prerequisite for heavy metals removal by Fe^0 (Guo et al., 2015). Additionally, the As removal rate was 48.3%, 61.9%, 90.8%, 71.9% and 52.7% in the combined- Fe^0/FeS_2 systems with ratios of 9:1, 4:1, 1:1, 1:4 and 1:9, respectively. It was interesting to find that As removal rates increased as the ratios were gradually close to 1:1 ($1:9 < 1:4 < 1:1$, $1:1 > 4:1 > 9:1$), and which achieved the highest As removal rate in the ratio of 1:1 system. What's more, the ratio systems of 1:9 and 1:4 of the FeS_2 -predominant systems exhibited higher As removal efficiency than the ratio systems of 9:1 and 4:1 of the Fe^0 -predominant systems (Fig.1b). This showed that FeS_2 was an inert As removal material while Fe^0 was an reactive one. More addition of FeS_2 in the combined- Fe^0/FeS_2 system led to higher enhancement of the reactivity of Fe^0 and ultimately resulted in higher As removal rate.

Fig.1 Effects of different compositions of Fe^0/FeS_2 (w/w) mixture on As removal (a) and As

removal rate (b), $[\text{As(III)}] = 2\text{mg L}^{-1}$, $[\text{Fe}^0 + \text{FeS}_2] = 1\text{g/L}$, $\text{pH} = 6.8$

3.2 Effects of mixture dosage

Batch experiments were conducted to determine the optimal dosage of the combined- Fe^0/FeS_2 mixtures for As removal under aerobic conditions (Fig.2a). The ratio of Fe^0 to FeS_2 was 1:1 and the solution contained 2 mg L^{-1} As(III) without pH adjustment ($\text{pH}_{\text{ini}} = 6.8$). The mixtures concentration of 0.2, 0.5, 0.8, 1.0 and 2.0 g L^{-1} were applied. Correspondingly, the As removal rates were 5.7%, 30.3%, 56.3%, 90.8% and 98.6% (Fig.2b). Results showed that the increasing dosage of the mixtures gave rise to a positive effect on As removal rate, and the optimal mixtures dosage for As removal was 2.0 g L^{-1} . With mixtures dosage increasing, more active sites and surface areas of Fe^0 and FeS_2 would be involved in reactions. Therefore, the enhancement effect of FeS_2 on the reactivity of Fe^0 would be strengthened and the removal of As would be improved.

Fig.2 Effects of different dosages (Fe^0+FeS_2) on As removal (a) and As removal rate (b), [As(III)]

$= 2 \text{ mg L}^{-1}$, $[\text{mFe}^0:\text{mFeS}_2] = 1:1$, $\text{pH} = 6.8$

3.3 Effects of different initial pH

The effects of different pH on As removal were investigated in the combined- Fe^0/FeS_2 ($\text{mFe}^0/\text{mFeS}_2 = 1:1$) systems and which were compared with the

single-FeS₂ systems and single-Fe⁰ systems.

Obviously, the single-FeS₂ systems were inert for As removal at different initial pH values (Fig.3a~3d). The removal rates were only 0.9%-5.0% at pH_{ini} 3.0-9.0 after 180 min. Sun et al (2012) found that the removal of As by FeS₂ was tightly related to the degree of FeS₂ oxidation. Therefore, the inefficient As removal efficiency by FeS₂ was probably related to its inert property of hardly being oxidized. However, the removal efficiency of As was observed to be highly pH dependent in the single-Fe⁰ systems. Approximately 100% of As was removed in 60 min at pH_{ini} 3.0 and in 120 min at pH_{ini} 5.0. Whereas only 49.2% of As was removed at pH_{ini} 6.8 and 22.2% at pH_{ini} 9.0 after 180 min. This phenomenon was consistent with previous study that developed by Sun et al (2014). As we all know, surface corrosion is a prerequisite for heavy metals removal by Fe⁰ (Guo et al., 2015). So the corrosion of pristine oxide film coated on Fe⁰ surface would be the first key step for Fe⁰ to remove As from water. In acidic and weakly acidic solutions (pH_{ini} 3.0-5.0), direct involvement of H⁺ would contribute to fast breakdown of pristine oxide film coated on Fe⁰ surface and rapid corrosion of Fe⁰ (Wei et al., 2016). Therefore, mass of iron hydroxide/oxide precipitations would be generated from the process of Fe⁰ corrosion, and which were mainly responsible for As sequestration. However, when the solution pH_{ini} were near-neutral and alkaline (pH_{ini} 6.8-9.0), the As removal efficiency would be primarily limited by the slow dissolution of pristine oxide film and authigenic passivation of Fe⁰ (Wei et al., 2016; Sun et al., 2016; Liang et al., 2014). Therefore, the As removal rates were low in single-Fe⁰ system at pH_{ini} 6.8 and 9.0. Totally, it could be drawn that

though there were some limitations for Fe^0 to remove As from aqueous solution, Fe^0 in the combined- Fe^0/FeS_2 system was an relatively effective As removal material and FeS_2 was an inert one. The pristine oxide film and the Fe^0 authigenic passivation were the major limitations that deteriorated As removal efficiency under neutral and alkaline conditions.

Compared with the single- Fe^0 system and single- FeS_2 system, the combined- Fe^0/FeS_2 systems ($m\text{FeS}_2/m\text{Fe}^0 = 1:1$) exhibited more excellent As removal performance. Specifically, when pH_{ini} were 3.0 and 5.0, which were the better conditions for Fe^0 to rapidly remove As from aqueous solution, the As removal rates of the combined- Fe^0/FeS_2 system were almost the same as the single- Fe^0 systems (Fig.3a,3b). Owing to the fact that the dosage of Fe^0 was half in the combined- Fe^0/FeS_2 system, the close As removal rates in the combined- Fe^0/FeS_2 systems and single- Fe^0 systems indicated that the reactivity of Fe^0 in the combined- Fe^0/FeS_2 systems had been enhanced at pH_{ini} 3.0 and 5.0. Moreover, when initial pH values were 6.8 and 9.0, the As removal rates were 90.8% and 67.0% in the combined- Fe^0/FeS_2 systems respectively, compared with only 49.2% and 22.2% in the single- Fe^0 systems at the same conditions (Fig.3c,3d). It showed that the reactivity of Fe^0 in the combined- Fe^0/FeS_2 systems had also been significantly enhanced at pH_{ini} 6.8 and 9.0. Therefore, it could be drawn that the combination of Fe^0 and FeS_2 could contribute to the effective As removal within a broad pH range (3.0-9.0). In addition, the difference in As removal rate between the combined- Fe^0/FeS_2 systems and single- Fe^0 systems increased with the increasing pH_{ini} values (41.6%-44.8%). This

suggested that the combined- Fe^0/FeS_2 system was more reactive for As removal in more alkaline conditions. FeS_2 in the combined- Fe^0/FeS_2 probably enhanced the corrosion of Fe^0 and thereby improved the As removal efficiency.

Fig.3 Effects of different pH_{ini} on As removal, (a) $\text{pH} = 3.0$, (b) $\text{pH} = 5.0$, (c) $\text{pH} = 6.8$ and (d) $\text{pH} = 9.0$, $[\text{As(III)}] = 2\text{mg L}^{-1}$, $[\text{mFe}^0:\text{mFeS}_2] = 1:1$

3.4 Mechanism of the enhancement of FeS_2 on Fe^0 corrosion

3.4.1 Fe^{2+} release with and without 1,10-phenanthroline addition and pH variations

As discussed in part 3.1-3.3, the higher As removal rate in combined- Fe^0/FeS_2 system was probably resulted from the enhanced corrosion of Fe^0 by addition of FeS_2 . To verify the enhanced corrosion and explore the enhancement mechanism of FeS_2 on Fe^0 corrosion in the combined- Fe^0/FeS_2 system, evolutions of pH and Fe^{2+} release with and without 1,10-phenanthroline addition were examined. The experiments with

1,10-phenanthroline addition were conducted to determine the release of total Fe ion in aqueous solution, since Fe^{2+} and 1,10-phenanthroline could rapidly form a stable complex once Fe^{2+} was released (Liang et al., 2013). The experiments without 1,10-phenanthroline addition were conducted to determine the presence of Fe^{2+} in aqueous solution during the actual reaction process.

Obviously, there was no manifest change of Fe^{2+} and total Fe ion released in single- FeS_2 systems at different pH_{ini} values (3.0-9.0) (Fig.4). It suggested that the oxidation of FeS_2 in aqueous solution was very slow (Eq.2). Owing to the oxidation of FeS_2 always has a great influence on As removal (Bulut et al., 2014), so As removal in single- FeS_2 was inefficient. This was consistent with the results of the As removal experiment. Consequently, it could be known that FeS_2 in the combined- Fe^0/FeS_2 systems was inert to be oxidized and it contributed little to As removal due to its inert properties.

Of particular interest, there were some interesting differences in the release of Fe^{2+} and total Fe ion between the combined- Fe^0/FeS_2 system and single- Fe^0 system. When pH_{ini} was 3.0, the release of Fe^{2+} went down sharply in the single- Fe^0 system after 5 min but not until after 15 min in the combined- Fe^0/FeS_2 system. Besides, after 15 min, higher release of Fe^{2+} and slower increase of pH (from 3.0 to 5.6 in the combined- Fe^0/FeS_2 system vs from 3.0 to 6.1 in the single- Fe^0 system) attended in the combined- Fe^0/FeS_2 system at the whole time. This indicated that authigenic passivation (passivated by Fe^0 corrosion products) of Fe^0 occurred more latter in the

combined Fe^0/FeS_2 system. Meanwhile, it also revealed that the corrosion of Fe^0 had been enhanced by the addition of FeS_2 . Generally, galvanic effects could occur in suspensions of electrically conducting minerals that with different reduction potential (Nowak et al., 1984). Herein, FeS_2 possesses a more positive standard reduction potential (+ 0.35 V) than Fe^0 (- 0.44 V) (Lü et al., 2019). Therefore, a galvanic couple of Fe^0/FeS_2 was probably formed by this big potential difference driven (0.79 V), where FeS_2 was cathode and Fe^0 was anode. The electron transfer of anode material would be accelerated when the galvanic couples had been formed between two different materials. Thus, it could be inferred that FeS_2 in the combined- Fe^0/FeS_2 system probably acted as a cathode material, which accelerated the electrons transfer from Fe^0 to authigenic passivation layer and promoted the passivation layer to breakdown. Therefore, the authigenic passivation was alleviated in the combined- Fe^0/FeS_2 system. Since FeS_2 owns a high reduction potential, such similar galvanic couple effects were very common in suspensions of FeS_2 and other minerals (ZnS , PbS , CuS , CuFeS_2), where FeS_2 acted as an cathode that promoted the enhanced corrosion of low-potential mineral (Santos et al., 2016). Besides, previous study also showed that the galvanic couple could be occurred between Fe^0 (- 0.44 V) and passivated Fe^0 (+ 0.57 V), where Fe^0 with low potential was the anode and passivated Fe^0 with high potential was the cathode. When mixing them together, the removal of *p*-nitrophenol would be obviously enhanced due to the galvanic corrosion of Fe^0 (Yi et al., 2017), whose reaction mechanism was similar to our work. So the enhanced reactivity of Fe^0 in the combined- Fe^0/FeS_2 system might also be ascribed to the

galvanic couples between Fe^0 and FeS_2 .

In addition, compared with the single- Fe^0 system, there were less total Fe ion and more Fe^{2+} have been detected in the combined- Fe^0/FeS_2 system. The difference between Fe^{2+} and total Fe ion was mainly resulted from the oxidation and hydrolysis of Fe^{2+} , while the products generated from the oxidation and hydrolysis of Fe^{2+} could adsorb As from the solution. So it could be drawn that there was less Fe^{2+} being oxidized and hydrolyzed in the combined- Fe^0/FeS_2 system for the As removal. Considering that As removal speed of the single- Fe^0 system and combined- Fe^0/FeS_2 system were almost the same, so we speculated that there were some corrosion products responsible for As removal must be generated via other pathways. Basically, non-proton consumption reactions probably were the primarily involvement in this corrosion process in the combined- Fe^0/FeS_2 system (Eq.3-4) (Sun et al., 2014; Manning et al., 2002). That is, some corrosion products that generated through direct reactions between Fe^0 , O_2 and H_2O were also responsible for As removal. Therefore, a conclusion could be drawn that electron transfer from Fe^0 to O_2 was accelerated by introducing FeS_2 in the combined- Fe^0/FeS_2 system. This phenomenon supported the galvanic corrosion effect of Fe^0/FeS_2 . At the anode, Fe^0 lost electrons and was oxidized. At the cathode, FeS_2 acted as electron mediator that accelerated the electron transfer between Fe^0 and O_2 . Moreover, lower pH values in the combined- Fe^0/FeS_2 system at the whole reaction time were also supported the involvement of non-proton consumption reactions, because some non-proton consumption reactions could simultaneously generate iron (hydroxide) oxide products and H^+ (Eq.3-4). When pH_{ini}

334 was 5.0, the variations of Fe^{2+} and total Fe ion release in the single- Fe^0 system and
335 combined- Fe^0/FeS_2 system showed almost the same trend as the case of pH_{ini} 3.0. It
336 indicated that the corrosion mechanism of Fe^0 enhanced by FeS_2 in
337 combined- Fe^0/FeS_2 system at pH_{ini} 5.0 was almost the same as pH_{ini} 3.0.

Fig.4 The variations of Fe^{2+} and total Fe ion release and pH evolutions at different pH_{inis} in single- FeS_2 system, single- Fe^0 system and the combined- Fe^0/FeS_2 system

However, when pH_{ini} was 6.8, variations of pH values, the release of Fe^{2+} and total Fe ion in the combined- Fe^0/FeS_2 system and single- Fe^0 system were significantly different from the case of pH_{ini} were 3.0 and 5.0. The release of Fe^{2+} was very low in the single- Fe^0 system and combined- Fe^0/FeS_2 system (less than 1 mg L^{-1}), which was primarily related to the dominant Fe species that were affected by pH values (6.5~6.8) (Katsoyiannis et al., 2008). However, the release of total Fe ion was more in the combined- Fe^0/FeS_2 system of interest than that of the single- Fe^0 system. This result directly confirmed that the enhanced corrosion of Fe^0 was also involved in the combined- Fe^0/FeS_2 system under near-neutral condition (pH_{ini} 6.8). Considering that the slow dissolution of pristine oxide film coated on Fe^0 surface was the key factor that always inhibited the Fe^0 corrosion under neutral and alkaline conditions (Guo et al., 2015; Liang et al., 2014), so the role of FeS_2 in the combined- Fe^0/FeS_2 system was ascribed to improving decomposition of the pristine oxide film. Previous studies showed that breakdown of pristine oxide film occurred when Fe^0 contacted with water, whereby water and electrons from Fe^0 participated in the reduction of oxide film (Sun et al., 2016). Therefore, the improved decomposition of the pristine oxide film in the combined- Fe^0/FeS_2 system mainly depended on the accelerated electron release from Fe^0 to oxide film layer by addition of FeS_2 . This effect was linked to the role of FeS_2 as a cathode, because FeS_2 as a cathode could accelerate the electrons to release from Fe^0 when they contacted with each other, and thereby accelerated the reduction decomposition of the pristine oxide film. Therefore, the corrosion of Fe^0 would be enhanced and the As removal rate

would be increased. In addition, pH values decreased from 6.8 to 5.8 in the combined-Fe⁰/FeS₂ system at first 5 min, indicating that non-proton consumption reactions should be also involved in corrosion processes (Eq.3-4), because these reactions could simultaneously generated iron corrosion products for As removal and H⁺ for declining the pH values. The higher As removal rate and lower pH values in the combined-Fe⁰/FeS₂ system suggested that no-proton consumption reactions has been accelerated by the addition of FeS₂. That is, electron transfer between Fe⁰ and O₂ mediated by FeS₂ under near-neutral conditions was accelerated. At pH_{ini} 9.0, the variations of Fe²⁺, total Fe ion and pH in the combined-Fe⁰/FeS₂ system were also almost similar to those of pH_{ini} 6.8, which revealed the same roles played by FeS₂ in the combined-Fe⁰/FeS₂ system.

3.4.2 Characterization analysis

A series of characterizations of Fe⁰ and FeS₂ before and after reaction were investigated in this study. The reactions were all proceeded under near-neutral conditions (pH_{ini} = 6.8).

SEM (Scanning Electron Microscope) was used to investigate the surface morphology of Fe⁰ and FeS₂ before and after reaction. As shown in Fig.5, the ground FeS₂ before reaction had different sizes and different shapes. After reaction, there were no obvious changes observed on surface of it. However, the situation of Fe⁰ was different from FeS₂. The pristine Fe⁰ was irregular and agglomerated with many small particles, and the surface of it was rather smooth. After Fe⁰ was physically mixed with FeS₂, no obvious changes have occurred on their surface. While after reaction, the

surface of Fe^0 obtained from the single- Fe^0 system was corroded into some pits and with some few oxidation products covering on it. More notably, the Fe^0 obtained from the combined- Fe^0/FeS_2 system showed more serious surface corrosion and there were more conspicuous corrosion products covering on it. These results further indicated that FeS_2 was relatively inert to be oxidized while Fe^0 was with high reactivity. FeS_2 in the combined- Fe^0/FeS_2 system could promote the surface corrosion of Fe^0 . The results were consistent well with our front points.

Fig.5 SEM images of Fe^0 and FeS_2 before and after reaction in different systems

Oxidant products were not detected by XRD (X-ray diffraction) characterization (Fig.6), which was probably related to their low levels and amorphous structure. But interestingly, an additional diffraction peaks of $2\theta = 28.2^\circ$ (PDF#40-0475) corresponding to Fe-O-As hydrate was observed in mixture from the combined- Fe^0/FeS_2 system. It indicated that besides adsorption on iron (hydroxide)

oxides, co-precipitation of As with iron (hydroxide) oxides was also involved in the As removal process in the combined- Fe^0/FeS_2 system. Additionally, it was obvious seen that the peak signal of Fe^0 in the combined- Fe^0/FeS_2 system was weaker than it was in single- Fe^0 system (Fig.6). This suggested that more Fe^0 was involved in the corrosion reaction process and finally led to less iron to be existed in the combined- Fe^0/FeS_2 system. It also revealed that the enhanced corrosion of Fe^0 was attended in the combined- Fe^0/FeS_2 .

Fig.6 XRD patterns of reacted Fe^0 and FeS_2 in the single- FeS_2 system, single- Fe^0 system and combined- Fe^0/FeS_2 system; black ● was FeS_2 , green ● was Fe^0 , purple ● was quartz sand and * was Fe-O-As hydrate

The XPS (X-ray photoelectron spectroscopy) spectrums of reacted products were also investigated, elements of Fe, C, O and As were detected in these three systems and element S was detected in the combined- Fe^0/FeS_2 system and single- FeS_2 system (Supplementary Fig.S2). The spectrums of Fe (2p) were showed in Fig.6a, the peak at 706.7 ± 0.1 eV was assigned to Fe(II)-S , and the peaks of 710.6 ± 0.1 eV, 712.6 eV, 719.1 ± 0.1 eV, 724.64 eV were assigned to Fe(III)-O species (Yamashita and Hayes,

2008; Tan, 2016; Lin, 1997) (Fig.7a). There were no sulfur species binding with Fe(III) being found on reacted mixture of Fe^0 and FeS_2 , indicating that there was no complete oxidation of FeS_2 was involved in the combined- Fe^0/FeS_2 system. With comparison of Fe (2p) spectrum of the single- Fe^0 system and combined- Fe^0/FeS_2 system, it was found that fitting parameters were almost the same while the peaks intensities were different. Peaks intensities were stronger in the combined- Fe^0/FeS_2 system than those in single- Fe^0 system. It means that more iron (hydroxide) oxides were generated on the surface of Fe^0/FeS_2 mixture in the combined- Fe^0/FeS_2 system. The reason of this phenomenon could be accounted for the acceleration of reactions between Fe^0 , O_2 and H_2O in aqueous solution. The S (2p) spectrum of reacted FeS_2 was fitted with peaks at 162.3 eV, 163.4 eV and 168.8 eV, which corresponded to bulk S_2^{2-} dimers originated from FeS_2 , S_n^{2-} generated from incomplete oxidation of FeS_2 , and SO_4^{2-} resulted from complete oxidation of FeS_2 , respectively (Fig.7c) (Dong et al., 2013; Yang et al., 2014). As expected, no SO_4^{2-} signal was detected in the reacted mixtures of Fe^0 and FeS_2 , which suggested that the complete oxidation of FeS_2 was absent in the combined- Fe^0/FeS_2 system (Eq.2). This result was consistent well with analysis of spectrums of Fe (2p). Additionally, determination of aqueous SO_4^{2-} concentration showed the same result (Supplementary Fig.S3). Following the above, it could be known that FeS_2 was just inert material in the combined- Fe^0/FeS_2 system and enhanced the corrosion of Fe^0 while without its own complete oxidation. Therefore, FeS_2 in the combined- Fe^0/FeS_2 system could be considered as cathode electron mediator, of which accelerated the electron transfer between Fe^0 and pristine oxide

440 film, passivation film as well as O_2 , and thereby enhanced the corrosion of Fe^0 .
 441 Besides, the As (3d) spectrum of reacted products (Fe^0 , FeS_2 , Fe^0/FeS_2 mixture) was
 442 also examined (Fig.7b). The spectrum was fitted well with peaks at 45.5 ± 0.1 eV
 443 (As(III)) and at 44.6 ± 0.1 eV (As(V)). Result showed that As(III) oxidation was also
 444 participated in As removal process, the reason of this occurrence could be explained
 445 by Fenton-like reactions involved in $Fe^0/H_2O_2/O_2$ and $FeS_2/H_2O_2/O_2$ systems (Sun et
 446 al., 2014; Zhang et al., 2015).

447
 448 **Fig.7** XPS spectrum of Fe-(a), As-(b) and S-(c) of reacted Fe^0 and FeS_2 in the single- FeS_2 system,
 449 single- Fe^0 system and combined- Fe^0/FeS_2 system

4 Conclusion

This study has investigated the enhanced effect of FeS_2 on Fe^0 corrosion for As removal in a combined- Fe^0/FeS_2 system. Results showed that the combination of FeS_2 and Fe^0 could significantly enhance the As removal rate and the combined- Fe^0/FeS_2 system could be proceeded within a broad pH range (3.0~9.0). The improved As removal in the combined- Fe^0/FeS_2 system was primarily attributed to the being enhanced corrosion of Fe^0 by addition of FeS_2 . The mechanism study showed that FeS_2 in the combined- Fe^0/FeS_2 system could alleviate the passivation of Fe^0 (pH_{ini} 3.0~5.0) and accelerate the dissolution of pristine oxide film coated on Fe^0 surface (pH_{ini} 6.8~9.0). Besides, FeS_2 in combined- Fe^0/FeS_2 system could accelerate the electron transfer between Fe^0 and O_2 . Therefore, it was proposed that FeS_2 in the combined- Fe^0/FeS_2 system acted as catalytic cathode, which formed a galvanic couple with Fe^0 . Once they contacted each other in aqueous solution, FeS_2 could accelerate electron release from Fe^0 to pristine oxide film (pH_{ini} 3.0~5.0) and authigenic passivation layer (pH_{ini} 6.8~9.0) as well as O_2 , and thereby enhanced the corrosion of Fe^0 and promoted more generation of corrosion products for efficient As removal.

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References

- Bissen M. and Frimmel F. H., 2003. Arsenic-a Review. Part II: Oxidation of Arsenic and its Removal in Water Treatment. *CLEAN-Soil, Air, Water*. 31 (2), 97-107.
- Bulut., Gülay., Yenial., Ünzile., Emiroglu., Emrecan and Sirkeci A. A., 2014. Arsenic removal from aqueous solution using pyrite. *J. Clean. Prod.* 84 (1), 526-532.
- Chernyshova I. V., 2004. Pyrite Oxidation Mechanism in Aqueous Solutions: An in situ FTIR Study. *Russ. J. Electrochem.* 40 (1), 69-77.
- Christen K., 2001. The arsenic threat worsens. *Environ. Sci. Technol.* 35 (13), 286A-291A.
- Clancy T. M., Hayes K. F. and Raskin L., 2013. Arsenic Waste Management: A Critical Review of Testing and Disposal of Arsenic-Bearing Solid Wastes Generated during Arsenic Removal from Drinking Water. *Environ. Sci. Technol.* 47 (19), 10799-10812.
- Dhar R. K., Zheng Y., Rubenstone J. and Geen A. V., 2004. A rapid colorimetric method for measuring arsenic concentrations in groundwater. *Anal. Chim. Acta*. 526 (2), 203-209.
- Dong J., Zhao Y., Zhao R and Zhou R., 2010. Effects of pH and particle size on kinetics of nitrobenzene reduction by zero-valent iron. *J. Environ. Sci.* 22 (11), 1741-1747.
- Dong S. H., Jin K. S., Batchelor B. and Abdel-Wahab A., 2013. Removal of arsenite(As(III)) and arsenate(As(V)) by synthetic pyrite (FeS_2): Synthesis, effect of contact time, and sorption/desorption envelopes. *J. Colloid Interface Sci.* 392 (4), 311-318.
- Fan D., Lan Y., Tratnyek P. G., Johnson R. L., Filip J., O'Carroll D. M., Nunez A. G. and Agrawal A., 2017. Sulfidation of Iron-Based Materials: A Review of Processes and Implications for Water Treatment and Remediation. *Environ. Sci. Technol.* 51 (22), 13070-13085.
- Garelick H., Jones H., Dybowska A. and Valsami-Jones E., 2008. Arsenic pollution sources. *Rev. Environ. Contam. T.* 197, 17-60.
- Geiger C. L., Ruiz N. E., Clausen C. A., Reinhart and Quinn J. W., 2002. Ultrasound pretreatment of elemental iron: kinetic studies of dehalogenation reaction enhancement and surface effects. *Water Res.* 36 (5), 1342-1350.
- Guan X., Sun Y., Qin H., Li J., Lo I. M. C., He D. and Dong H., 2015. The limitations of applying zero-valent iron technology in contaminants sequestration and the corresponding countermeasures: The development in zero-valent iron technology in the last two decades (1994-2014). *Water Res.* 75, 224-248.
- Guo X., Zhe Y., Dong H., Guan X., Ren Q., Lv X. and Xin J., 2015. Simple Combination of Oxidants with Zero-Valent-Iron (ZVI) Achieved Very Rapid and Highly Efficient Removal of Heavy Metals from Water. *Water Res.* 88, 671-680.
- Huang S., Xu C., Shao Q., Wang Y., Zhang B., Gao B., Zhou W. and Tratnyek P. G., 2018.

- 507 Sulfide-modified zerovalent iron for enhanced antimonite sequestration: Characterization,
508 performance, and reaction mechanisms. *Chem. Eng. J.* 338, 539-547.
- 509 Iaea I. A. E. A., 2012. Arsenic Contamination of Groundwater in Bangladesh. *Iwmi Working*
510 *Papers.* (30), 6791-6800.
- 511 Kanel S. R., Manning B., Charlet L. and Choi H., 2005. Removal of arsenic(III) from groundwater
512 by nanoscale zero-valent iron. *Environ. Sci. Technol.* 39 (5), 1291-1298.
- 513 Katsoyiannis I. A., Ruettimann T. and Hug S. J., 2008. pH dependence of Fenton reagent
514 generation and As(III) oxidation and removal by corrosion of zero valent iron in aerated water.
515 *Environ. Sci. Technol.* 42 (19), 7424-7430.
- 516 Ke B., Li Y., Chen J., Zhao C. and Chen Y., 2016. DFT study on the galvanic interaction between
517 pyrite (100) and galena (100) surfaces. *Appl. Surf. Sci.* 367, 270-276.
- 518 Lackovic J. A., Nikolaidis N. P. and Dobbs G. M., 2000. Inorganic Arsenic Removal by
519 Zero-Valent Iron. *Eviron. Eng. Sci.* 17 (1), 29-39.
- 520 Leupin O. X. and Hug S. J., 2005. Oxidation and removal of arsenic (III) from aerated
521 groundwater by filtration through sand and zero-valent iron. *Water Res.* 39 (9), 1729-1740.
- 522 Li J., Qin H., Zhang W. X., Shi Z., Zhao D. and Guan X., 2016. Enhanced Cr(VI) Removal by
523 Zero-valent Iron Coupled with Weak Magnetic Field: Role of Magnetic Gradient Force. *Sep.*
524 *Purif. Technol.* 176, 40-47.
- 525 Li J., Zhang X., Sun Y., Liang L., Pan B. C., Zhang W. and Guan X., 2017. Advances in
526 Sulfidation of Zerovalent Iron for Water Decontamination. *Environ. Sci. Technol.* 248, 173-182.
- 527 Liang L., Sun W., Guan X., Huang Y., Choi W., Bao H., Li L. and Jiang Z., 2014. Weak magnetic
528 field significantly enhances selenite removal kinetics by zero valent iron. *Water Res.* 49 (1),
529 371-380.
- 530 Liang L., Yang W., Guan X., Li J., Xu Z., Wu J., Huang Y. and Zhang X., 2013. Kinetics and
531 mechanisms of pH-dependent selenite removal by zero valent iron. *Water Res.* 47 (15),
532 5846-5855.
- 533 Lin T. C., 1997. A consistent method for quantitative XPS peak analysis of thin oxide films on
534 clean polycrystalline iron surfaces. *Appl. Surf. Sci.* 119 (1), 83-92.
- 535 Lü Y., Li J., Li Y., Liang L., Dong H., Chen K., Yao C., Li Z., Li J. and Guan X., 2019. The roles
536 of pyrite for enhancing reductive removal of nitrobenzene by zero-valent iron. *Appl. Catal.*
537 *B-Environ.* 242, 9-18.
- 538 Lü Y., Li Z., Li J., Chen K., Dong H., Shou J. and Li Y., 2018. Synergetic effect of pyrite on
539 Cr(VI) removal by zero valent iron in column experiments: An investigation of mechanisms.
540 *Chem. Eng. J.* 349, 522-529.
- 541 Manning B. A., Hunt M. L., Amrhein C. and Yarmoff J. A., 2002. Arsenic(III) and arsenic(V)
542 reactions with zerovalent iron corrosion products. *Environ. Sci. Technol.* 36 (24), 5455-5461.
- 543 Min X., Li Y., Ke Y., Shi M., Chai L. and Xue K., 2017. Fe-FeS₂ adsorbent prepared with iron

- 544 powder and pyrite by facile ball milling and its application for arsenic removal. *Water Sci.*
545 *Technol.* 76 (1), 192-200.
- 546 Nowak P., Krauss E. and Pomianowski A., 1984. The electrochemical characteristics of the
547 galvanic corrosion of sulphide minerals in short-circuited model galvanic cells. *Hydrometallurgy.*
548 12 (1), 95-110.
- 549 Pagnanelli F., Moscardini E., Giuliano V. and Toro L., 2004. Sequential extraction of heavy
550 metals in river sediments of an abandoned pyrite mining area: pollution detection and affinity
551 series. *Environ. Pollut.* 132 (2), 189-201.
- 552 Rajajayavel S. R. and Ghoshal S., 2015. Enhanced reductive dechlorination of trichloroethylene
553 by sulfidated nanoscale zerovalent iron. *Water Res.* 78, 144-153.
- 554 Ramos M. A. V., Yan W., Li X., Koel B. E. and Zhang W., 2009. Simultaneous Oxidation and
555 Reduction of Arsenic by Zero-Valent Iron Nanoparticles: Understanding the Significance of the
556 Core-Shell Structure. *J. Phys. Chem. C.* 113 (33), 14591-14594.
- 557 Randle T. H., 1994. Galvanic Corrosion-A Kinetic Study. *J. Chem. Educ.* 71 (3), 261-265.
- 558 Santos E. D. L., Rivera-Santillán R. E., Talavera-Ortega M. and Bautista F., 2016. Catalytic and
559 galvanic effects of pyrite on ferric leaching of sphalerite. *Hydrometallurgy.* 163, 167-175.
- 560 Schlegel A. and Wachter P., 1976. Optical properties, phonons and electronic structure of iron
561 pyrite (FeS₂). *Journal of Physics C Solid State Physics.* 9 (17), 3363-3369.
- 562 Smedley P. L. and Kinniburgh D. G., 2002. A review of the source, behaviour and distribution of
563 arsenic in natural waters. *Appl. Geochem.* 17 (5), 517-568.
- 564 Sun F., Dempsey B. A. and Osseo-Asare K. A., 2012. As(V) and As(III) reactions on pristine
565 pyrite and on surface-oxidized pyrite. *J. Colloid Interface Sci.* 388 (1), 170-175.
- 566 Sun Y., Guan X., Wang J., Meng X., Xu C. and Zhou G., 2014. Effect of Weak Magnetic Field on
567 Arsenate and Arsenite Removal from Water by Zerovalent Iron: An XAFS Investigation. *Environ.*
568 *Sci. Technol.* 48 (12), 6850-6858.
- 569 Sun Y., Li J., Huang T. and Guan X., 2016. The influences of iron characteristics, operating
570 conditions and solution chemistry on contaminants removal by zero-valent iron: A review. *Water*
571 *Res.* 100, 277-295.
- 572 Tan P., 2016. Active phase, catalytic activity, and induction period of Fe/zeolite material in
573 nonoxidative aromatization of methane. *J. Catal.* 338, 21-29.
- 574 Wai C M., Wang J S., Yang M H., 2002. Arsenic Contamination of Groundwater, Blackfoot
575 Disease, and Other Related Health Problems[J]. *ACS Sym Ser.* 835:210-231.
- 576 Wei X., Zhang B., Tao Z., Wu X. and Mao J., 2016. An insight in magnetic field enhanced
577 zero-valent iron/H₂O₂ Fenton-like systems: Critical role and evolution of the pristine iron oxides
578 layer. *Sci Rep.* 6, 24094.
- 579 Xu C., Zhang B., Zhu L., Lin S., Sun X., Jiang Z. and Tratnyek P. G., 2016. Sequestration of
580 Antimonite by Zerovalent Iron: Using Weak Magnetic Field Effects to Enhance Performance and

- 581 Characterize Reaction Mechanisms. Environ. Sci. Technol. 50 (3), 1483-1491.
- 582 Yamashita T. and Hayes P., 2008. Analysis of XPS spectra of Fe^{2+} and Fe^{3+} ions in oxide
583 materials. Appl. Surf. Sci. 254 (8), 2441-2449.
- 584 Yan W., Herzing A. A., Kiely C. J. and Zhang W. X., 2010. Nanoscale zero-valent iron (nZVI):
585 aspects of the core-shell structure and reactions with inorganic species in water. J. Contam.
586 Hydrol. 118 (3-4), 96-104.
- 587 Yang Z., Kang M., Ma B., Xie J., Chen F., Charlet L. and Liu C., 2014. Inhibition of U(VI)
588 Reduction by Synthetic and Natural Pyrite. Environ. Sci. Technol. 48 (18), 10716-107124.
- 589 Yi, R., Li, J., Yuan, D. and Bo, L., 2017. Removal of p-nitrophenol (PNP) in aqueous solution by
590 the mixed Fe^0 /(passivated Fe^0) fixed bed filters. Industrial & Engineering Chemistry Research. 56,
591 9293-9302.
- 592 Zhang L., Qin X., Tang J., Liu W. and Yang H., 2016. Review of arsenic geochemical
593 characteristics and its significance on arsenic pollution studies in karst groundwater, Southwest
594 China. Appl. Geochem. 77, 80-88.
- 595 Zhang Y., Tran H. P., Hussain I., Zhong Y. and Huang S., 2015. Degradation of p -chloroaniline
596 by pyrite in aqueous solutions. Chem. Eng. J. 279, 396-401.

Highlights

- Combined Fe^0 and FeS_2 resulting in the highest As removal efficiency.
- FeS_2 enhancing the corrosion of Fe^0 within a broad pH range.
- FeS_2 promoted the decomposition of pristine oxide film and passivation film of Fe^0 .
- FeS_2 acted as cathode which accelerated electron release from Fe^0 .