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Authors
Liu, Wei
Liu, Jia
Zhou, Peipei
et al.

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Mechanisms for hydroxyl radical production and arsenic removal in sulfur-vacancy greigite (Fe₃S₄)

Wei Liu a,c, Jia Liu a, Peipei Zhou a, Randy A. Dahlgren d, Xuedong Wang a,b,*

a Zhejiang Provincial Key Laboratory of Watershed Science and Health, College of Public Health and Management, Wenzhou Medical University, Wenzhou 325035, China
b National and Local Joint Engineering Laboratory of Municipal Sewage Resource Utilization Technology, School of Environmental Science and Engineering, Suzhou University of Science and Technology, Suzhou 215009, China
c Key Laboratory for Green Chemical Process of Ministry of Education, School of Chemical Engineering and Pharmacy, Wuhan Institute of Technology, Wuhan 430205, China
d Department of Land, Air and Water Resources, University of California, Davis, CA 95616, United States

Abstract

Herein, we systematically investigated the mechanisms of OH production and arsenic (As(III)) oxidation induced by sulfur vacancy greigite (Fe₃S₄) under anoxic and oxic conditions. Reactive oxygen species analyses revealed that sulfur vacancy-rich Fe₃S₄ (SV-rich Fe₃S₄) activated molecular oxygen to produce hydrogen peroxide (H₂O₂) via a two-electron reduction pathway under oxic conditions. Subsequently, H₂O₂ was decomposed to OH via the Fenton reaction. Additionally, H₂O was directly oxidized to OH by surface high-valent iron (Fe(IV)) resulting from the abundance of sulfur vacancies in Fe₃S₄ under anoxic/oxic conditions. These differential OH-generating mechanisms of Fe₃S₄ resulted in higher OH production of SV-rich Fe₃S₄ compared to sulfur vacancy-poor Fe₃S₄ (SV-poor Fe₃S₄). Moreover, the OH production rate of SV-rich Fe₃S₄ under oxic conditions (19.3 ± 1.0 μM·h⁻¹) was 1.6 times greater than under anoxic conditions (11.8 ± 0.4 μM·h⁻¹). As(III) removal experiments and X-ray photoelectron spectra (XPS) showed that both OH production pathways were favorable for As(III) oxidation, and a higher concentration of As(V) was immobilized on the surface of SV-rich Fe₃S₄ under oxic conditions. This study provides new insights concerning OH production and environmental pollutants removal mechanisms on surface defects of Fe₃S₄ under anoxic and oxic conditions.

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1. Introduction

Hydroxyl radical (·OH) is a strong oxidant owing to its high standard reduction potential (2.8 eV), and plays a pivotal role in environmental chemistry, geochemistry, and life sciences [1]. For example, ·OH can directly mineralize organic pollutants and natural organic matter (NOM) to CO₂ [2], and alter microbial structure and metabolic processes [3]. Hydroxyl radicals also impact human health, such as ·OH formation as a byproduct of mineral oxidation that contributes to pneumoconiosis in coal miners [4]. Hydroxyl radicals are not only produced via photolysis of NOM in the atmosphere, surface waters and oceans, but also by redox reactions between naturally-occurring minerals and oxygen or water [5–8]. Thus, it is important to elucidate ·OH production mechanisms in natural environments.

Iron-based materials, including zero-valent iron (ZVI) and iron sulfides, are widely used as efficient activators for ·OH production ascribing to their redox reactivity [9–12]. Mechanisms for ·OH generation are a function of mineral structure and ambient environmental conditions. For instance, ZVI serves as an electron donor for molecular oxygen (O₂) activation via a two-electron transfer pathway to generate hydrogen peroxide (H₂O₂). Furthermore, structural ferrous ions (∼Fe(II)) in iron-based materials may first reduce O₂ to superoxide anions (O₂⁻) via a single-electron transfer pathway, with the O₂⁻ subsequently reduced to H₂O₂ via a single-electron transfer route [13–15]. The generated H₂O₂ then decomposes to ·OH by reaction with Fe(II) via the Fenton reaction. Moreover, contributions of these two O₂ activation pathways are mediated by competing ligands [12,16].

Recent studies verified the role of surface defects in iron minerals as efficient activation sites for ·OH production. For example, nonstoichiometric Fe(III) sites resulting from sulfur-deficient defects in pyrite directly oxidized H₂O to ·OH under anoxic conditions [17]. He et al. demonstrated that ·OH produced via reaction of Fe(III) and H₂O on pyrite under visible light irradiance and anoxic conditions resulted in antimony (Sb(III)) oxidation [18]. However, most natural minerals ordinarily experience alternating oxic and anoxic conditions, ascribing to the strong O₂ perturbations in subsurface environments [19]. Thus, past studies provide evidence for ·OH production by both O₂ activation and H₂O oxidation pathways in natural environments under oxic and anoxic conditions. For instance, Yuan et al. [20] systematically evaluated the mechanism of ·OH production from pyrite oxidation under oxic and anoxic conditions, and documented that more ·OH was generated from H₂O oxidation on sulfur-deficient sites of pyrite surfaces under anoxic conditions. The authors demonstrated that the predominant ·OH generation pathway was identified as the two-electron transfer route under oxic conditions [20].

Greigite (Fe₃S₄), as an intermediate phase on the transformation pathway of Fe₃S₄ to pyrite, forms during early diagenetic stages involving sedimentary sulfate reduction [21–23]. Given the important role of Fe₃S₄ in environmental chemistry and geochemistry, many studies explored the effects of Fe₃S₄ on the fate and transport of environmental compounds. For example, heavy metals such as antimony (Sb(III)/Sb(V)) and lead (Pb(II)) could be efficient adsorbed on Fe₃S₄ surface, which significantly decreased their mobility and toxicity [24,25]. Moreover, hydrogen peroxide (H₂O₂) and peroxysulfate (SO₅²⁻) were adsorbed on the surface of Fe₃S₄ where they were sequentially activated to ·OH and SO₅²⁻ for bisphenol and atrazine degradation [26,27]. Thus, naturally-occurring Fe₃S₄ may impact several related remediation processes of environmental pollutants.

Our previous studies demonstrated that Fe₃S₄ efficiently reduced Cr(VI) and roxarsone, owing to the coupled reductive abilities of structural ferrous and sulfide moieties [28–30]. Importantly, the surface structure of Fe₃S₄ can be tuned by synthesis methods to enhance various functional applications [31–33]. In spite of the previous studies investigating iron-sulfide materials, there is a paucity of information regarding specific ·OH production pathways associated with Fe₃S₄ and the efficacy of utilizing ·OH production by Fe₃S₄ for oxidation of environmental pollutants.

Arsenic, as a redox metallod, occurs naturally in soils and rocks and is widely used in industry and agriculture [34]. Due to the dissolution out of rock or industrial release, high levels of arsenic were often detected in ground water [35]. As the specific interaction of iron sulfides and As(III), and high stabilization of the formed As–Fe–S products [36], it is promising to involve Fe₃S₄ for As(III) removal. Herein, we aim to elucidate the effects of sulfur vacancies in Fe₃S₄ (greigite) on ·OH production mechanisms and As(III) removal under both oxic and anoxic conditions. Cumulative ·OH production from Fe₃S₄ was quantified via the probe reaction between benzoic acid (BA) and ·OH to generate p-hydroxybenzoic acid (p-HBA). A series of trapping agents were used to evaluate the contribution of reactive oxygen intermediates to ·OH production. Specific molecular probe experiments quantified the concentrations of iron species (Fe(II), Fe(III), and Fe(IV)) and reactive oxygen species to rigorously characterize reaction pathways. As such, this study provides fundamental mechanistic information concerning ·OH production pathways by Fe₃S₄ and highlights potential applications for environmental remediation.

2. Experimental section

2.1. Sample preparation

Sulfur-vacancy (SV) Fe₃S₄ nanosheets were synthesized using a one-step solvothermal method [31,37]. In the SV-rich Fe₃S₄ synthesis process, 0.834 g FeSO₄·7H₂O was dissolved in 30 mL of ethylene glycol (EG) to form solution I, and 0.363 g l-cysteine was dissolved in 30 mL of EG to form solution II. Solution I was added dropwise into solution II within 5 min and stirred at room temperature for 20 min to form a bright red mixture. The resulting solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 12 h. After cooling to room temperature, a black product was collected by centrifugation and sequential washed with deionized water and ethanol three times before drying in a vacuum oven at 60 °C for 6 h. The SV-poor Fe₃S₄ was synthesized following identical methods, but using water rather than EG as the solvent.

2.2. ·OH production from Fe₃S₄

A mixed solution of benzoic acid/piperazine-N,N'-bis(2-ethane sulfonic acid) (BA/PIPES) was prepared by dissolving 1.220 g BA and 0.906 g PIPES into 1 L deionized water. PIPES were selected because they do not complex with Fe(III) and Fe(II). The pH of the mixture was adjusted to 6.7 ± 0.1 using 1 mM NaOH. This stock solution was stored in the dark to avoid potential photochemical reactions. Oxic experiments were carried out in 50 mL conical flasks containing 20 mL BA/PIPES stock solution and a desired dosage of Fe₃S₄. Flasks were covered with aluminum foil and shaken with a rotary shaker (SPH-100B, Shiping, China) at 150 rpm and 25 °C. For anoxic experiments, the BA/PIPES solution was purged with ultrapure argon gas for 1 h to remove dissolved oxygen, and then transferred into a two-necked flask. To avoid oxygen contamination in the reactor, the two-necked flask was connected with an argon filled balloon and rubber stopper.
Samples were withdrawn at a regular time interval from the flask with a 2-mL syringe. As the reaction rate constant for BA and ‘OH (\(k_{\text{BA-OH}} = 5.7 \times 10^4 \text{M}^{-1} \text{s}^{-1}\)) is much higher than that for PIPES and ‘OH, the consumption of ‘OH by PIPES was ignored [38]. Quenching experiments were carried out with additions of 2,2’-bipyridine (BPY, 10 mM), superoxide dismutase (SOD, 600 U/mL) and catalase (CAT, 2450 U/L) to the reaction process. Samples were passed through a 0.22 μm polytetrafluoroethylene (PTFE) filter to remove residual Fe₃S₄. All experiments were carried out in triplicate.

2.3. As(III) oxidation by SV-rich Fe₃S₄

To demonstrate the application of ‘OH production by SV-Fe₃S₄ for remediation of environmental pollutants, As(III) was selected as a model pollutant. Briefly, the As(III) standard solution was diluted into PIPES (3 mM, pH 6.7 ± 0.1) to form a 10 mg/L As(III) stock solution. A 0.02 g mass of SV-rich Fe₃S₄ and 40 mL As(III) stock solution were transferred into the aforementioned reactor under oxic or anoxic conditions. The reactor was shaken with a rotary shaker (SPH-100B, Shiping, China) at 150 rmp and 30 °C. Samples were passed through a 0.22 μm PTFE filter and 500 μL methanol (6 M) added to quench further reaction between As(III) and ‘OH. All experiments were carried out in triplicate.

3. Results and discussion

3.1. Characterization of S-vacancy Fe₃S₄

Figure S1a shows powder X-ray diffraction (XRD) patterns for Fe₃S₄ synthesized using EG and H₂O as the solvent. Diffraction peaks for both samples are well indexed to the cubic phase of Fe₃S₄ (No.16-173), verifying successful synthesis of Fe₃S₄ crystals. As EG favors the formation of surface defects in nanomaterials [39], S vacancies were characterized using EPR spectra (Figure S1b). A typical signal with a g factor of 2.003 identifies the existence of S vacancies in Fe₃S₄ synthesized using EG and H₂O as solvent. Notably, the signal intensity of Fe₃S₄ synthesized using EG as solvent was much higher than that of Fe₃S₄ synthesized with H₂O solvent. These results document that SV-rich Fe₃S₄ and SV-poor Fe₃S₄ were obtained from the solvothermal synthesis process using EG and H₂O as solvents, respectively. The morphology of Fe₃S₄, characterized by scanning electron microscopy (SEM) and transmission electron microscope (TEM), exhibited a sheet-like character with a thickness of ~10 nm for both samples, and a distinct bending in the SV-rich Fe₃S₄ structure (Figure S2). These characterization results were consistent with our previous work [37].

3.2. ‘OH production with SV-Fe₃S₄

The ‘OH production by SV-Fe₃S₄ was quantified using BA/PIPES solution under oxic conditions. Cumulative ‘OH production by SV-rich Fe₃S₄ gradually increased to 138.9 μM within 8 h (Fig. 1). In contrast, ‘OH production for SV-poor Fe₃S₄ was below the detection limit (0.59 μM) of the high performance liquid chromatography (HPLC) method revealing the importance of sulfur vacancies in promoting ‘OH production under oxic conditions. The Brunauer Emmett-Teller (BET) surface areas were calculated to be 20.0 and 17.7 m²/g for the SV-rich Fe₃S₄ and SV-poor Fe₃S₄, respectively, which were corresponded to the average pore volumes of 10.1 and 10.8 nm [37]. These slight differences of BET surface areas and average pore volumes between the SV-poor Fe₃S₄ and SV-rich Fe₃S₄ ruled out the specific contributions of surface area and pore volume to the ‘OH formation efficiency. Moreover, cumulative ‘OH production by SV-rich Fe₃S₄ under anoxic conditions gradually increased to 98.0 μM within 8 h, which was considerably lower than production (138.9 μM) under oxic conditions (Fig. 1). Cumulative ‘OH production curves for SV-rich Fe₃S₄ under both oxic and anoxic conditions followed a pseudo-zero-order kinetic model. The apparent ‘OH generation rate constant for SV-rich Fe₃S₄ under oxic conditions (19.3 ± 1.0 μM h⁻¹) was 1.6 times greater than the rate under anoxic conditions (11.8 ± 0.4 μM h⁻¹) (Table S1). Thus, we conclude that SV-rich Fe₃S₄ generates ‘OH production under both oxic and anoxic conditions, but ‘OH generation rates are a function of dissolved oxygen concentration.

The dependence of ‘OH production on the dosage of SV-rich Fe₃S₄ was evaluated for Fe₃S₄ doses of 0.5–3.0 g/L. Cumulative ‘OH concentrations increased with increasing reaction time to 8 h (Fig. 2). Final ‘OH concentrations increased from 30.7 and 13.2 μM to 138.9 and 98.0 μM as SV-rich Fe₃S₄ dosage increased from 0.5 to 3.0 g/L under oxic and anoxic conditions, respectively (Table S2). These concentrations correspond to ‘OH production rate increases from 3.9 ± 0.2 and 1.7 ± 0.2 μM h⁻¹ to 19.3 ± 1.0 and 11.8 ± 0.4 μM h⁻¹ (Table S2), respectively. The ‘OH production rates under oxic and anoxic conditions were linearly dependent on the dosage of SV-rich Fe₃S₄ (Fig. 2c). The slope under oxic conditions (7.0 ± 0.8 μmol h⁻¹ g⁻¹) was notably higher than for anoxic conditions (4.0 ± 0.1 μmol h⁻¹ g⁻¹), indicating the importance of molecular oxygen in the reaction processes.

3.3. Mechanism of ‘OH production by SV-rich Fe₃S₄

‘OH can be generated with iron-based materials via three pathways: (1) a two-step single-electron transfer from Fe(II) to oxygen generating O₂ and H₂O₂, with the H₂O₂ subsequently decomposed by Fe(II) via the Fenton reaction to generate ‘OH; (2) a direct two-electron transfer from iron-based materials to oxygen generating H₂O₂ and subsequent Fenton reaction; and (3) the oxidation of H₂O to ‘OH by surface defects or high-valence iron ions (such as Fe(IV)) [40]. To clarify the ‘OH production mechanism(s) induced by SV-rich Fe₃S₄ under oxic and anoxic conditions, we applied different scavengers (SOD for O₂, BPY for Fe(II), and CAT for H₂O₂) to capture the suspected reactive species involved in the ‘OH production process. The ‘OH production rates were not depressed in the presence of SOD under oxic conditions, suggesting that O₂ was not an important component in the reaction pathway (Figure S3). Thus, we rule out the pathway for a direct two-step single-electron transfer from Fe(II) to oxygen for the generation of O₂ and H₂O₂ by SV-rich Fe₃S₄ under oxic conditions. In contrast, ‘OH production was much higher than that of Fe₃S₄ synthesized with H₂O solvent. These results document that SV-rich Fe₃S₄ and SV-poor Fe₃S₄ were obtained from the solvothermal synthesis process using EG and H₂O as solvents, respectively. The morphology of Fe₃S₄, characterized by scanning electron microscopy (SEM) and transmission electron microscope (TEM), exhibited a sheet-like character with a thickness of ~10 nm for both samples, and a distinct bending in the SV-rich Fe₃S₄ structure (Figure S2). These characterization results were consistent with our previous work [37].

Fig. 1. Cumulative concentrations of ‘OH under different conditions induced by S-vacancy Fe₃S₄. The dosage of Fe₃S₄ was 3.0 g/L.
production rates markedly decreased from 19.3 ± 1.0 to 0.4 ± 0.2 and 1.6 ± 0.1 μM h⁻¹ with the addition of BPY and CAT, respectively (Fig. 3a and Table S3). This confirms that oxic OH production processes by SV-rich Fe₃S₄ involve Fe(II) and H₂O₂. These data provided compelling evidence that oxygen is efficiently activated by SV-rich Fe₃S₄ via a two-electron transfer route to generate H₂O₂ rather than a single-electron transfer route to generate O₂. Similarly, OH production rates under anoxic conditions were depressed by BPY and CAT (Fig. 3b), further revealing the significant role of Fe(II) and H₂O₂ in OH production in the absence of oxygen.

Next, we quantified the role of Fe species (Fe(II) and Fe(III)) in OH production pathways. Fe(II) concentrations increased from 0.003 and 0.004 to 0.696 and 0.490 mM at 8 h as the dosage of SV-rich Fe₃S₄ increased from 0.5 to 3.0 g/L under oxic and anoxic conditions, respectively (Figure S4). The higher Fe(II) concentration under oxic conditions was attributed to more efficient redox facilitated dissolution of SV-rich Fe₃S₄ in the presence of dissolved oxygen. Correspondingly, all Fe(III) concentrations under both oxic and anoxic conditions were lower than the detection limit (<0.007 mM) (Figure S5) owing to the low solubility of Fe(III) at pH 7.0.

To further evaluate the effects of iron species on OH production processes under oxic and anoxic conditions, the solid-phase products were separated and characterized by XPS. The high-resolution spectra of Fe 2p in pristine SV-rich Fe₃S₄ displayed four peaks at 707.6, 710.3, 711.5, and 712.8 eV (Figure S6), which were assigned to surface Fe(II)-S and structural Fe(II)-S, Fe(III)-S, and Fe(III)-O, respectively [41,42]. The relative fraction of Fe(II)surf decreased from 5.8% to 3.2% after anoxic reaction, indicating release and partial Fe(II) oxidation under anoxic conditions. Meanwhile, Fe(II)surf markedly disappeared after oxic reaction, suggesting enhanced oxidation of Fe(II)surf in the presence of oxygen. Correspondingly, the relative fraction of Fe(III)-O increased from 18.3% to 23.7% and 25.6% under anoxic and oxic conditions, respectively. The increase in Fe(III)-O confirms Fe(II) oxidation to generate Fe(III) in both oxic and anoxic pathways.

As H₂O₂ is a key intermediate for OH production via the Fenton reaction, we quantified H₂O₂ concentrations in BA/PIPES solution at SV-rich Fe₃S₄ dosages of 0.5–3.0 g/L under oxic and anoxic conditions. H₂O₂ concentrations sharply increased to 2.6, 1.6, and 2.0 μM at 2 h as the SV-rich Fe₃S₄ dosage increased from 0.5 to 3.0 g/L under oxic conditions (Fig. 3c). These results confirm the efficient production of H₂O₂ in the presence of SV-rich Fe₃S₄ and oxygen. Subsequently, H₂O₂ concentrations decreased to 0.9, 1.7 and 1.9 μM after 8 h of reaction as SV-rich Fe₃S₄ dosages increased. The prominent decrease in instantaneous H₂O₂ concentrations for the 0.5 g/L SV-rich Fe₃S₄ treatment indicates that the H₂O₂ generation rate induced by Fe₃S₄ was lower than the H₂O₂ decomposition rate via the Fenton reaction at lower Fe₃S₄ dosages. Instantaneous H₂O₂ concentrations were independent of SV-rich Fe₃S₄ mass at higher doses. This may result from rapid consumption of H₂O₂ via the Fenton reaction in the presence of high concentrations of Fe(II) released from redox promoted dissolution of SV-rich Fe₃S₄ at higher solid-phase concentrations. In contrast, instantaneous H₂O₂ concentrations gradually increased to ~0.7 μM for all SV-rich Fe₃S₄ dosages (0.5–3.0 g/L) under anoxic conditions (Fig. 3d). The H₂O₂ concentrations generated under anoxic conditions were notably lower than those under oxic conditions. Thus, we conclude that H₂O₂ generation induced by SV-rich Fe₃S₄ was strongly dependent on the dissolved oxygen concentration.

To further clarify the effects of H₂O₂ on OH production with SV-rich Fe₃S₄ under oxic and anoxic conditions, we evaluated OH production upon spiking with H₂O₂. The OH concentration increased from 138.9 to 241.3 μM with the addition of 5 mM H₂O₂ under oxic conditions (Fig. S7a). The large increase in OH concentration may be attributed to an enhancement of the Fenton reaction by increased availability of ferrous ions via redox promoted dissolution of SV-rich Fe₃S₄ in the presence of oxygen (Figure S4). In contrast, a much smaller increase in OH concentrations occurred (98.0 to 131.3 μM) upon addition of 5 mM H₂O₂ under anoxic conditions (Figure S7b). This differential response to H₂O₂ additions suggests a less important role for the Fenton reaction generation of OH under anoxic conditions.

Given the importance of dissolved oxygen (DO) in redox reactions, we monitored DO concentrations during OH production by SV-rich Fe₃S₄ under oxic and anoxic conditions using a DO probe (JPB-607A, Shanghai INESA). The initial DO concentration
(8.3 mg/L) was up to its saturated concentration (8.3 mg/L) at 25 °C, confirming the undersaturated of DO in the solution. However, it decreased to 7.4 mg/L after 1 h and maintained a concentration of 7.2 ± 0.2 mg/L for the remaining 7 h of reaction in the system open to the atmosphere (Figure S8). The initial decrease in DO was caused by the higher oxygen-consumptive rate than the reaeration rate into the reaction chamber. To further demonstrate oxygen consumption by reactions with SV-rich Fe3S4, we constrained the open system with a rubber stopper to record oxygen consumption. In the isolated system, DO concentration gradually decreased to ~5.0 mg/L within 8 h. These results confirmed the role of molecular oxygen in OH production by SV-rich Fe3S4 under oxic conditions.

DO concentrations were also monitored under anoxic conditions to follow OH production by SV-rich Fe3S4. DO concentrations were lower than 0.5 mg/L throughout the 8 h reaction period providing confirmation that molecular oxygen is not required for OH production in the SV-rich Fe3S4 system (Figure S8). The production of OH in the SV-rich Fe3S4 system under anoxic conditions probably acquires an oxygen atom from H2O molecules. To verify this assumption, we examined the isotopic distribution of p-HBA-obtained from the reaction of H218O-enriched solution and SV-rich Fe3S4 in the BA/PIPES system under anoxic conditions. The prominent ion peak at m/z of 141.0543 confirmed that p-HBA-18O was generated when using H218O as the solvent (Figure S9). These results confirm that the oxidation of H2O was the source of the oxygen used to generate OH in the SV-rich Fe3S4 system under anoxic conditions.

Finally, we examined whether H2O was oxidized to generate OH by ferryl ions (Fe(IV)) in association with the sulfur defects on iron-based materials. Methyl phenyl sulfoxide (PMSO) was used as a molecular probe for detection of Fe(IV) during the SV-Fe3S4 oxidation process [43]. HPLC chromatograms revealed a new peak with a retention time of 6.8 min that matched the PMSO2 standard solution (Figure S10). These results provide strong support for the generation of Fe(IV) released from SV-rich Fe3S4. PMSO2 concentrations gradually increased to 7.2 and 4.9 μM within 8 h in the presence of SV-rich Fe3S4 under both oxic and anoxic conditions (Figure 4). The higher Fe(IV) concentrations are consistent with the higher OH concentrations generated in the presence of oxygen. In sharp contrast, PMSO2 concentrations were lower than 2.3 μM when using SV-poor Fe3S4 under oxic and anoxic conditions. This indicates that Fe(IV) is preferentially generated by SV-rich Fe3S4 providing strong evidence that both surface defects and oxygen favor Fe(IV) release from Fe3S4.

Synthesizing our results, we propose mechanistic pathways for production of OH by SV-rich Fe3S4 under oxic and anoxic conditions (Scheme 1). First, Fe(IV) released from SV-rich Fe3S4 directly oxidizes H2O to generate OH under both oxic and anoxic conditions. Subsequently, the OH partially self-binds to form H2O2. The H2O2 generated in these processes is finally decomposed by Fe(II) to produce OH via the Fenton reaction.

3.4. Removal of As(III) by reaction with SV-rich Fe3S4

To demonstrate the potential for oxidation of environmental pollutants by OH, we systematically investigated As(III) removal by SV-rich Fe3S4 under oxic and anoxic conditions. As(III) concentrations sharply decreased from 10 to ~0.01 mg/L within 120 min under both oxic and anoxic conditions (Fig. 5a). As As
(III) removal by heterogeneous materials involves adsorption, oxidation and co-precipitation processes. Dissolved As(V) concentrations were monitored throughout the reaction period. In all cases, dissolved As(V) concentrations were less than the detection limit (0.01 μg/L), indicating negligible accumulation of As(V) in the solution phase, but rather As retention on the solid-phase. After that, the contributions of different reactive species to As(III) removal were subsequently investigated in detail. Figure S11 shows that As(III) could not be removed with H₂O₂ alone under oxic and anoxic conditions, ruling out the direct oxidation of As(III) with H₂O₂. Furthermore, under oxic conditions, the As(III) removal efficiencies with SV-rich Fe₃S₄ were 59.3% and 61.3%, respectively, in the presence of methanol and isopropanol. Correspondingly, they were 59.2% and 60.2%, respectively, under anoxic conditions. Consequently, we posit that partial As(III) could be efficiently adsorbed or oxidized on the surface of SV-rich Fe₃S₄ surface, and As(III) oxidation mainly resulted from ‘OH rather than Fe(IV).

To assess As interactions with the SV-rich Fe₃S₄ surface, the solid-phase was isolated following reaction and then reacted with a phosphate solution to desorb surface bound As(III) and As(V). The masses of As(III) and As(V) desorbed from the SV-rich Fe₃S₄ surface under oxic conditions were 12.5 and 25.5 μg, respectively (Fig. 5b). The higher concentration of As(V) than As(III) confirms the significant contribution of As(III) oxidation in the overall As(III) removal process. Under anoxic conditions, the masses of As(III) and As(V) desorbed from the SV-rich Fe₃S₄ were 18.1 and 3.3 μg, respectively. Thus, under anoxic conditions, As(III) is preferentially adsorb on the SV-rich Fe₃S₄ surface rather than being oxidized to As(V) and subsequently adsorbed. The lower mass of As(V) desorbed under anoxic conditions confirms the lower oxidative ability of SV-rich Fe₃S₄ under anoxic conditions. These findings are fully consistent with ‘OH production dynamics with SV-rich Fe₃S₄ under oxic and anoxic conditions.

Importantly, the mass of total As desorbed from SV-rich Fe₃S₄ surfaces under anoxic (21.3 μg) and oxic (38.0 μg) conditions...
was much lower than the fortified As mass (200 μg). This discrepancy suggests the formation of other As-containing species (i.e., strongly surface bound or co-precipitated phases) on the surface of the SV-rich Fe₃S₄. To distinguish surface associated As materials, the reacted SV-rich Fe₃S₄ was collected and characterized by XPS. The XPS spectra of As 3d was fitted by individual curves with peaks at 45.5 and 44.2 eV, attributable to As(V) and As(III), respectively (Fig. 5c) [44]. This analysis corroborates a higher relative fraction of As(V) under oxic (80.7%) than anoxic (77.2%) conditions and reflects the strong As(III) oxidative ability of SV-rich Fe₃S₄, especially under oxic conditions. Therefore, SV-rich Fe₃S₄ has the remarkable capacity to oxidize and retain As under both oxic and anoxic conditions.

4. Conclusions

In summary, this study demonstrated that magnetic Fe₃S₄ with sulfur vacancies achieved high ·OH production rates and As(III) oxidation/retention capabilities under both anoxic and oxic conditions. To further the application of SV-Fe₃S₄ for environmental applications, we systematically elucidated the ·OH production mechanisms and its efficacy for As(III) remediation. Experimental results confirmed that sulfur vacancies accelerated the formation of high-valent iron that in turn facilitated the direct oxidation of H₂O to produce ·OH under anoxic conditions. Additionally, structural ferrous ions in Fe₃S₄ activate molecular O₂ to generate H₂O₂ and promote subsequent Fenton reaction for ·OH production. This work enhances our mechanistic understanding of ·OH production and As(III) oxidation/retention and highlights the prospects of synthesizing structurally-defective, iron-based minerals to optimize remediation strategies. These ·OH-generating minerals have excellent potential for several environmental remediation applications, such as treatment of As(III)-polluted wastewater and degradation/transformation of organic pollutants.

CRediT authorship contribution statement

Wei Liu: Conceptualization, Methodology, Investigation, Writing – original draft, Funding acquisition. Jia Liu: Investigation, Validation, Visualization. Peipei Zhou: Software, Formal analysis. Randy A. Dahlgren: Writing – review & editing. Xuedong Wang: Funding acquisition, Project administration, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcis.2021.08.072.

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