



Enhanced degradation of chloramphenicol at alkaline conditions by S(-II) assisted heterogeneous Fenton-like reactions using pyrite



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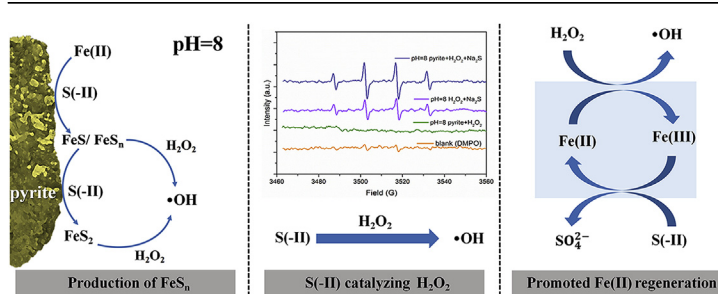
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HIGHLIGHTS

- S(-II) significantly enhanced efficiency of Fenton-like reaction at alkaline condition.
- The highly reactive FeS_n generated could catalyze H₂O₂ to produce •OH efficiently.
- •OH could be generated by the unrecognized S(-II)-H₂O₂ reactions.
- S(-II) could accelerate Fe(III)/Fe(II) by reducing Fe(III) to Fe(II).

GRAPHICAL ABSTRACT



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ABSTRACT

The Fenton-like reactions catalyzed by pyrite can efficiently degrade organic contaminants by oxidation process. When chloramphenicol (CAP) was exposed to the pyrite-H₂O₂ system, the CAP removal rate rapidly reached 100% however slowed to a halt at alkaline conditions. Results indicated that by adding S(-II) in pyrite-H₂O₂ system improved the oxidation efficiency of CAP at alkaline conditions. The transformation of S₂²⁻ and S_n²⁻ observed by X-ray photoelectron spectroscopy (XPS), confirmed that amorphous iron polysulfide (FeS_n) was freshly generated on the pyrite surface. The availability of S(-II) promoted the generation of FeS_n. Besides, S(-II) played a role in accelerating the Fe(III)/Fe(II) cycles. The potential of S(-II) activating H₂O₂ to generate hydroxyl radicals (•OH), which was confirmed by electron spin resonance (ESR) spectroscopy, quenching experiments, and trapping experiments, have supported the proposed mechanisms. This study came up with an efficient way of enhancing Fenton-like reactions by pyrite catalyzed at alkaline conditions, by adding S(-II) in the system. The new findings have implications for sulfide minerals, their interactions with pollutants, and the transformation products of sulfur in systems where Fe species are also present.

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1. Introduction

Pyrite (FeS₂) is the most abundant natural sulfur mineral in the

Earth's crust. It has attracted considerable attention as an effective semiconductor and promising material for thin-film solar cells. Through examining 23 promising semiconducting materials, pyrite stands out as a low-cost alternative for photovoltaics research (Wadia et al., 2009). Additionally, colloidal FeS₂ nanocrystal inks and nanostructured FeS₂ have been synthesized and used for thin-

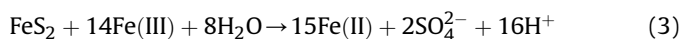
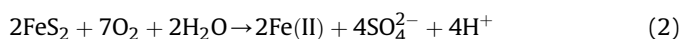
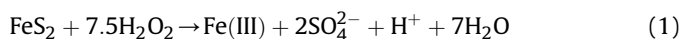
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film photovoltaics and LiSi/FeS₂ thermal batteries, respectively (Au, 2003; Puthusseray et al., 2010). Due to its electronic transmission capacity and crystalline structure, FeS₂ has been investigated extensively as an extraordinary heterogeneous Fenton catalyst (Sacchi et al., 2012) involved in the degradation of 2,4,6-trinitrotoluene (Matta et al., 2007), trichloroethylene (Che et al., 2011), carbon tetrachloride (Kriegman-King and Reinhard, 1994), pyrene (Choi et al., 2014) etc. In particular, a higher removal rate of trinitrotoluene has been observed in the pyrite-H₂O₂ reaction than that in the hematite/magnetite-H₂O₂ reaction (Arienzo, 1999). The pyrite-H₂O₂ reaction mechanisms are summarized as follows: (i) various radicals, such as •OH and •O₂⁻, are produced (Arienzo, 1999; Che and Lee, 2011); (ii) the continuous dissolution of iron ions from the pyrite surface and the simultaneous generation of protons both promote homogeneous Fenton reactions (de Brito Benetoli et al., 2012; Bae et al., 2013; Wu et al., 2013; Choi et al., 2014; Hao et al., 2014); and (iii) the autocatalytic reaction of FeS₂ with Fe(III) serves to maintain full dose of Fe(II) (Arienzo, 1999; Wu et al., 2015).

Almost all studies have attributed the pyrite-promoted degradation of pollutants solely to a series of reactions involving Fe. However, at alkaline conditions, the series reactions of Fe are restrained. In such cases, it is consequential to investigate the way of enhancing pyrite catalyzing Fenton-like reaction at alkaline conditions. Researchers found using complexing agents at alkaline conditions improved Fenton-like reactions by preventing the precipitation of Fe²⁺ and Fe³⁺. Chen et al. detected that glutamic acid (GLDA) could enhance pyrite catalyzing Fenton-like reaction at alkaline condition (Wu et al., 2016). Recently, many studies have found that the addition of S(-II) can significantly enhance the reaction efficiency of nanozerovalent iron. This sulfide-modified nanoscale zero-valent iron (nZVI) exhibits high reactivity in the degradation of halogenated organic compounds and heavy metal immobilization (Butler and Hayes, 2001; Kim et al., 2011, 2013). The positive impact of S(-II)-rich conditions in such reductive reactions is mainly attributed to the formation of highly reactive FeS and FeS₂ coating on the surface. Sulfurized limonite (FeOOH) was more effective than limonite in Fenton-like processes (Toda et al., 2014). Toda et al. ascribed the enhanced results to the generation of FeS₂ on the limonite surface.

It was deduced in previous studies that freshly generated iron-sulfur compounds on the mineral surface under sulfide conditions play a crucial role in catalyzing H₂O₂ (Butler and Hayes, 2001; Kim et al., 2011, 2013). However, this effect was only inferred without obtaining direct evidence. Besides, S(-II) reacts with H₂O₂ to produce sulfate under acidic conditions (Satterfield et al., 1954), but S(-II)-catalyzed production of radicals from H₂O₂ has never been reported. Few studies have investigated the influence of S(-II)-rich conditions in Fenton-like reactions, rather than using S(-II) to enhance the pollutants degradation at alkaline conditions, or investigated the role of sulfur in pyrite-H₂O₂ reactions, particularly the potential of sulfide to activate H₂O₂. In pyrite-H₂O₂ system, there is originally S existing. The transformation of sulfur and iron on pyrite surface has been investigated, as described below (Bonnissel-Gissing et al., 1998):



In the redox reactions above, the lattice S(-I) is completely oxidized to SO₄²⁻. Similarly, sulfur species of chalcopyrite (CuFeS₂) is transformed to elemental sulfur (S(0)) and disulfide (S₂²⁻) (Klauber

et al., 2001). Then, oxidation of the disulfide phase directly produces thiosulfate, which is then oxidized to sulfate (Klauber, 2003). Researches have revealed that by adding S(-II) during the reaction or doping S on the surface, the catalyzing reaction was improved. Various catalysts have been used including Fe₂O₃/Al₂O₃ catalysts (Sun et al., 2015), P and S dual-doped graphitic porous carbon (Patel et al., 2017). The catalysis was enhanced, because of the bonding between S and element on catalyst's surface, and the unique geometric structure of the catalytic sites. However, the gap was left in Fenton-like reaction by using pyrite, which itself contains S element. It can be inferred that the transformation of sulfur occurs through oxidation reactions and directly affects the surface properties of pyrite. By creating a S(-II)-rich condition, the degradation of organic contaminants is apparently enhanced.

Chloramphenicol (CAP), a broad-spectrum antibiotic drug, widely found in aqueous and soil environment, has been used as a target pollutant in this research. When Na₂S was added in pyrite-H₂O₂ system, which constituted S(-II)-rich solutions, the CAP degradation was accelerated especially at alkaline conditions. The objective of this study is to elucidate the effect of sulfur in pyrite-H₂O₂ reactions especially at alkaline conditions. CAP degradations by pyrite-H₂O₂ under alkaline conditions in both S(-II)-limited and S(-II)-rich solutions were investigated with the purpose of answering two particular questions: (i) what transformation of sulfur was likely prevailing in the reaction of pyrite with H₂O₂; and (ii) how the transformation of sulfur contributed to CAP degradation after adding S(-II) in the solution. The study aims to reveal the mechanism of S(-II) reacting at alkaline condition in pyrite catalyzing Fenton-like reactions, including fresh generation of amorphous iron polysulfide (FeS_n), S(-II)-induced catalytic Fenton-like reactions and S(-II)-accelerated Fe(III)/Fe(II) cycles. The study provided an efficient way to enlarge the pH range for pyrite catalyzing Fenton-like reaction and considerably enhanced the catalysis of pyrite-H₂O₂ in alkaline conditions.

2. Experimental section

2.1. Chemicals and materials

Pyrite was obtained from LvLing Chemical Industry Group Co., Ltd. (Jiangsu, China). Analytical-grade hydrochloric acid, sodium hydroxide, hydrogen peroxide (30%, w/w), sodium sulfide, tert butyl alcohol (TBA), benzoic acid (BA) and ferrous sulfate heptahydrate were supplied by Chemicals Corporation (Shanghai, China). HPLC-grade methanol and CAP were purchased from ANPEL Scientific Instrument Co., Ltd. (Shanghai, China). Solutions were prepared with 18 MΩ Milli-Q water from a Millipore system (Bedford, USA).

2.2. Oxidation procedures

200 mL CAP (50 mg/L) solutions contained appropriate amounts of pyrite with or without certain dosages of Na₂S, and then pH was adjusted by NaOH and HCl. The reaction started after adding H₂O₂, with magnetic stirring. At specific time intervals, 1 mL sample was withdrawn and 10 μL methanol was added to terminate the reaction. The samples were filtered through 0.45 μm filters (ANPEL Scientific Instrument Co. Ltd., Shanghai). All experiments were run in triplicates, and the data were averaged. The standard deviations were usually within 6% unless otherwise noted.

2.3. Analytical procedures

Both CAP and *p*-HBA were measured with an Agilent 1260 liquid chromatography system equipped with a quaternary solvent

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