

Article

Natural Pyrite as a Catalyst for a Fenton Reaction to Enhance Xanthate Degradation in Flotation Tailings Wastewater

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Abstract: The efficient treatment of mineral-processing wastewater has attracted soaring interest recently. This study's objective was to degrade xanthate from flotation tailings wastewater using a pyrite-catalyzed Fenton system. A sodium butyl xanthate (SBX) removal rate of more than 96% was achieved via the method under optimal conditions (a H_2O_2 concentration of 0.5 mM, a FeS_2 concentration of 0.5 g/L, an initial SBX concentration of 100 mg/L, and a natural pH of 9.36 ± 0.5), which is 12.85% higher than with a H_2O_2 system. An appropriate concentration of natural pyrite can act as a catalyst to significantly improve the oxidation capacity of H_2O_2 . Additionally, the results of electron paramagnetic resonance and quenching measurements suggest that hydroxyl radicals ($\bullet\text{OH}$) are the main active species in the H_2O_2 - FeS_2 system. The possible reaction mechanism is proposed. The H_2O_2 adsorbs onto the pyrite surfaces and reacts with Fe^{2+} , triggering the formation of $\bullet\text{OH}$ and Fe^{3+} . The $\bullet\text{OH}$ most likely attacks the SBX that adsorbs on the pyrite surface or exists in the solution and promotes the transformation of the SBX anion ($\text{C}_4\text{H}_9\text{OCS}_2^-$) into the intermediate butyl xanthate peroxide (BPX, $\text{C}_4\text{H}_9\text{OCS}_2\text{O}^-$). Finally, BPX intermediates are likely further oxidized to smaller products such as SO_4^{2-} , CO_2 , and H_2O under the ongoing attack of $\bullet\text{OH}$.

Keywords: xanthate wastewater; natural pyrite; catalyst; Fenton reaction; degradation mechanism



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1. Introduction

Froth flotation, on the basis of the different surface properties of minerals, has become the most common and effective beneficiation method for the separation, purification, and enrichment of valuable components in ore [1,2]. Xanthate is one of the most common organic-sulfur-based collectors for the froth flotation of sulfide ores as well as a multitude of oxidized ores [3,4]. It has been reported that the consumption of alkyl xanthate is expected to reach approximately 371,826,000 tons by 2025 [5]. However, the flotation circuit only consumes half of the alkyl xanthate amount, and the other half is discharged to tailing ponds [6]. It is well recognized that xanthate residue in flotation tailings wastewater can not only seriously pollute the ecological environment around the mining area, but it can also damage the human nervous system and liver system [7,8]. Furthermore, when recycling beneficiation wastewater, this remaining agent will affect the flotation index and cause adverse effects on the flotation selectivity of the minerals [9]. Thus, it is of great significance to effectively treat the residual xanthate in flotation wastewater for the sustainable development of the mineral-processing industry and for environmental protection.

Recently, environmental issues related to the mineral-processing industry have received increased attention from researchers. The efficient treatment of mineral-processing

wastewater is the focus of research in this field. Traditional processes have been developed to remove xanthate from flotation wastewater, including coagulation–flocculation [10], adsorption [11,12], biodegradation [13,14], and chemical oxidation [15]. On the other hand, there are still many issues in the treatment of flotation xanthate wastewater via traditional methods. For example, the methods of coagulation–flocculation and adsorption only transfer xanthate molecules from wastewater to solid products or adsorbents, and can produce secondary pollution [16,17]. The microbial method takes a long time to degrade xanthate wastewater [4]. The conventional chemical oxidation methods have an extremely low treatment efficiency, and the treated xanthate wastewater usually fails to meet emission standards for release into the environment [10]. Therefore, it is vitally important to develop a green and efficient method for solving the problem of flotation tailings wastewater pollution.

During the last few decades, efforts to treat mineral-processing wastewater via advanced oxidation processes (AOPs) have been ongoing [18–20]. The Fenton oxidation process, as a green oxidation technology, has attracted significant attention among AOPs due to its strong oxidative capacity for the degradation of organic contaminants [21,22]. The main reaction mechanism of the classic Fenton reaction induced by aqueous Fe^{2+} is well known to be the decomposition of H_2O_2 to $\bullet\text{OH}$ (2.76 V) [22–25] having a higher redox potential than ozone (2.07 V), permanganate (1.68 V), and persulfate (2.01 V) [26]. This makes the Fenton reaction more effective and thermodynamically feasible for the oxidative degradation of organic contaminants. Despite its strong oxidation capacity, the classic homogeneous Fenton reaction has some critical disadvantages such as the rapid precipitation of $\text{Fe}(\text{OH})_3$, which generates significant amounts of sludge and causes the early termination of the reaction. Thus, a low pH is always required [27]. Recently, heterogeneous iron sources such as zerovalent iron (ZVI) and Fe-containing minerals (ferrihydrite, hematite, goethite, lepidocrocite, magnetite, and pyrite) playing roles of surface catalysts have been used to produce hydroxyl radicals during the Fenton reaction instead of an aqueous iron source [28–31]. With advantages over classic Fenton reactions such as less iron sludge formation, a wider working pH range, and the possible recycling of the iron promoter, Fenton systems catalyzed by heterogeneous Fe-containing solid catalysts have received soaring attention [32–34].

Pyrite (FeS_2) is one of the most abundant sulfide minerals on the Earth and contains a high content of iron [35]. Pyrite can be considered as a catalyst for wastewater treatment due to its low cost and environmentally friendly characteristics. Many researchers have confirmed the cost-effectiveness of pyrite as a catalyst for the removal of water pollutants [36–39]. Farzaneh Rahimi et al. investigated pyrite nanoparticles derived from mine waste as efficient catalysts for the activation of persulfates for the degradation of tetracycline. The results demonstrated that PMS was activated by using pyrite, and the pyrite/PMS process significantly decreased the nephrotoxicity (90%) and hepatotoxicity (85%) effect of tetracycline [36]. Zhang used an enhanced Fenton system catalyzed by heterogeneous pyrite to degrade nitrobenzene. The results indicated that the appropriate Fe^{2+} concentration generated by constant dissolution from a pyrite surface and by recycling Fe^{3+} contributed to this enhancement [37]. Research reported by Hyeongsu Che showed that trichloroethylene (TCE) was oxidatively degraded by $\bullet\text{OH}$ in the pyrite Fenton system and its degradation kinetics was significantly enhanced by the catalysis of pyrite to form $\bullet\text{OH}$ by decomposing H_2O_2 [38]. Lian investigated the degradation of tris(2-chloroethyl) phosphate (TCEP) as a category of OPE by pyrite (FeS_2)-activated persulfate (PS). The results confirmed that nearly 100% degradation of TCEP was achieved after 120 min in the FeS_2 -PS system, and Fe^{3+} and Cl^- could accelerate the degradation rate of TCEP [39]. Although numerous studies have demonstrated that pyrite could be effectively used as a heterogeneous catalyst for the removal of organic compounds from water, currently, limited basic knowledge is available on the use of natural pyrite as a catalyst for the development of enhanced remediation technologies to treat environmental contaminants, especially xanthate organics in flotation tailings wastewater.

Accordingly, pyrite was selected as a heterogeneous iron source to activate the Fenton reaction for the degradation of xanthate in flotation tailings wastewater. The main goals of this study were as follows: (1) determining the catalytic potential of pyrite in activating H_2O_2 for the generation of reactive species; (2) evaluating various operational conditions (concentrations of pyrite, H_2O_2 , and SBX); (3) assessing the contribution of free radicals in degradation reactions; (4) proposing a possible degradation pathway. This study may provide a strong basis for the green and sustainable treatment of mineral-processing wastewater.

2. Materials and Methods

2.1. Materials and Reagents

Sodium butyl xanthate (SBX) was supplied by Zhuzhou Flotation Reagents Ltd., Zhuzhou, Hunan, China, with a purity of >98%. H_2O_2 (non-stabilized, 30 wt%) was purchased from Yunnan Jingrui Technology Co., Ltd., Yunnan, China. 5,5-dimethyl-1-pyrrolin-N-oxide (DMPO, >99%) and TBA (tert-butyl alcohol, >99%) were produced by the Aladdin Industrial Corporation, Shanghai, China. The DMPO was serviced as a hydroxyl radical ($\bullet\text{OH}$) trapping agent, and the TBA was used as a hydroxyl radical ($\bullet\text{OH}$) scavenger. Ultra-pure water (resistivity $1.83 \times 10^7 \Omega\cdot\text{cm}$) was acquired from a Milli-Q50 purification system (Billerica, MA, USA). The pure pyrite used in this experiment was mined from Yunnan, China, and was finely ground in an agate mortar to obtain a 200-mesh powder (particle size, <75 μm). The chemical composition of the pyrite samples was analyzed, and the results confirmed that the purity of the pyrite samples was over 95%, of which the Fe content was 45.39% and the S content was 52.58%. Additionally, the pyrite sample was further analyzed via powder X-ray diffraction (XRD) and only the signal from pyrite was observed (Figure 1).

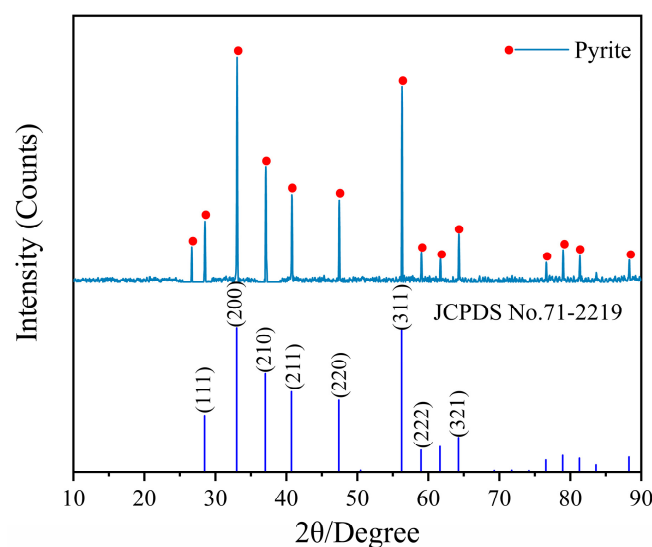


Figure 1. X-ray diffractograms of pyrite samples.

2.2. Degradation Experiments of Sodium Butyl Xanthate (SBX)

For the degradation experiments, 50 mL amounts of the various initial concentrations (50, 75, 100, 125, and 150 mg/L) of SBX solutions were used as simulated flotation tailing wastewater samples and were placed in a 150 mL beaker. The initial pH was 9.36 ± 0.5 . After that, certain amounts of H_2O_2 (if present) and pyrite catalyst (if present) were added into the solution to initiate the degradation reaction. Furthermore, the reaction system was stirred continuously with a magnetic stirrer at 500 rpm to ensure that the SBX solution was well mixed with the reagents and pyrite. Notably, no pH adjustment was performed in the whole process, and a pH meter (pH-25, Rex Electric Chemical) was used to measure the solution's pH value at the beginning and end of each experiment. All the experiments were

carried out at room temperature (25 °C). After a period of reaction (5~85 min), a part of the solution was filtered through a 0.45 µm pore size filter paper. Then, the filtrates were analyzed using an ultraviolet–visible (UV-vis) spectrophotometer. The absorbance of the filtrates was measured at 301 nm to investigate variations in the SBX concentrations during the degradation. The degradation efficiency of SBX was calculated using Equation (1):

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

where η (%) represents the degradation efficiency, C_0 (mg/L) is the initial concentration of SBX, and C_t (mg/L) is the SBX concentration after degradation.

2.3. Analytical Methods

UV full-spectrum scanning (UV-2700, Shimadzu, Japan; scanning range: 200–400 nm) was used to investigate variations in intermediates during SBX degradation. The concentrations of iron ions in the solutions were determined using the spectrophotometric method. Specifically, the standard solution of Fe^{2+} was prepared with ammonium ferrous sulfate, and the standard curve between Fe^{2+} concentrations and absorbances was established. Then, 10 mL of the reaction solution was added to a colorimetric tube. A volume of 1 mL of 50 mM hydroxylamine hydrochloride solution was added to the solution, reducing Fe^{3+} to Fe^{2+} , and the Fe^{2+} concentration was measured at 510 nm using a ferrozine method on the above-mentioned UV/visible spectrophotometer [40]. Also, the Fe^{3+} concentrations in the solution could be calculated based on the difference values between the total iron concentration and the Fe^{2+} concentration [41].

2.4. Capture of Active Species Experiments

The possible mechanism of SBX degradation was initially explored via a free radical capture test and electron paramagnetic resonance (EPR, Bruker, Germany). The EPR test was performed by using DMPO as the trapping agent to identify the generation of hydroxyl radicals ($\bullet\text{OH}$) in the H_2O_2 solution system and H_2O_2 - FeS_2 solution system. Additionally, TBA (200 mg/L) was added to the H_2O_2 - FeS_2 system to scavenge hydroxyl radicals for contrast testing with the aim of investigating the role of $\bullet\text{OH}$ in the SBX degradation.

3. Results and Discussion

3.1. The Degradation of SBX via the Pyrite-Catalyzed Fenton System

3.1.1. The Effect of H_2O_2 Concentration

The effect of H_2O_2 concentration on the degradation performance of SBX in the pyrite-catalyzed Fenton system was studied. The degradation conditions were as follows: $[\text{SBX}] = 100 \text{ mg/L}$, $[\text{FeS}_2] = 0.5 \text{ g/L}$, and initial $\text{pH} = 9.36 \pm 0.5$. As shown in Figure 2, the degradation efficiency of SBX increased with the increase in H_2O_2 concentration. When the H_2O_2 concentration was increased from 0.1 mM to 0.5 mM, the SBX degradation efficiency increased from 83.84% to 96.68% after 75 min of the reaction, which may be attributable to the increase in reactive groups (e.g., $\bullet\text{OH}$) produced by the reaction of Fe^{2+} with H_2O_2 to promote the degradation of SBX. When the H_2O_2 concentration was further increased from 0.5 mM to 0.9 mM, the SBS removal rate did not change remarkably. Prolonging the reaction time favored the SBX degradation, and the degradation efficiency changed weakly when the reaction time exceeded 75 min. Thus, 0.5 mM H_2O_2 was selected as the optimal reaction concentration in the subsequent experiments.

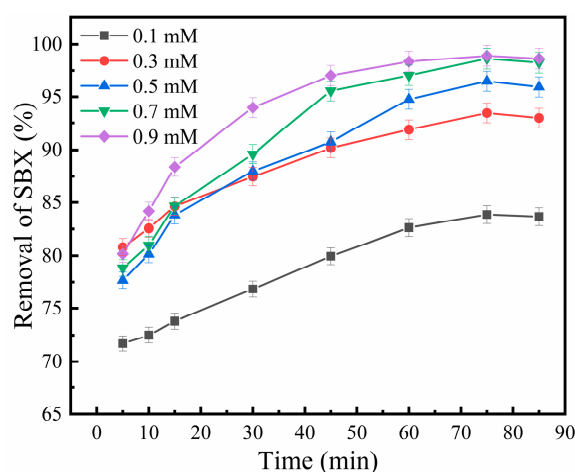


Figure 2. Effect of H_2O_2 concentration on the removal rate of SBX (conditions: $[\text{SBX}] = 100 \text{ mg/L}$, $[\text{FeS}_2] = 0.5 \text{ g/L}$, and initial $\text{pH} = 9.36 \pm 0.5$).

3.1.2. The Effect of Pyrite Concentration

The effect of the pyrite concentration on the removal rate of SBX is displayed in Figure 3 (conditions: $[\text{SBX}] = 100 \text{ mg/L}$, $[\text{H}_2\text{O}_2] = 0.5 \text{ mM}$, and initial $\text{pH} = 9.36 \pm 0.5$). As can be seen in Figure 3, the pyrite concentration played an important role in the removal rate of SBX. When the pyrite concentration increased from 0.1 g/L to 0.7 g/L , the removal rate of SBX increased during the reaction time ranging from approximately 5 to 45 min. With the further increase in the reaction time to 85 min, the removal rate of SBX with 0.7 g/L pyrite addition decreased to some extent. Notably, the removal rate of SBX with 0.9 g/L pyrite addition exhibited lower values than the corresponding results with 0.7 g/L pyrite addition. The results indicate that the excess addition of pyrite was detrimental to the SBX degradation. It is well accepted that the presence of pyrite can activate the decomposition of H_2O_2 [42]. This is rooted in the fact that pyrite provides iron ions and creates a heterogeneous Fenton system. The main chemical reactions involved are as follows [42,43]:

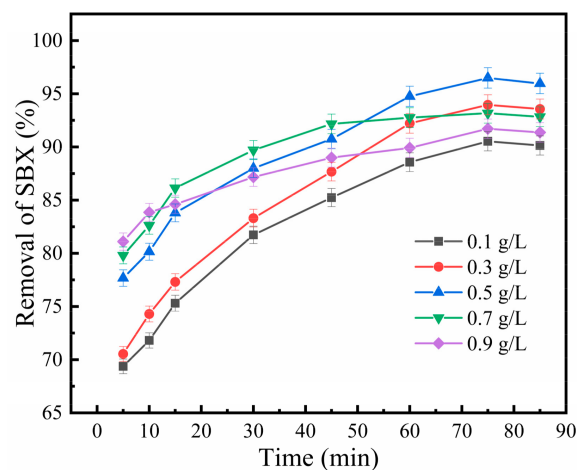
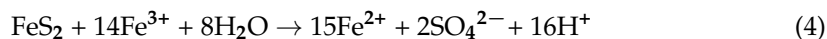
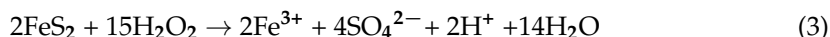


Figure 3. Effect of pyrite concentration on the removal rate of SBX (conditions: $[\text{SBX}] = 100 \text{ mg/L}$, $[\text{H}_2\text{O}_2] = 0.5 \text{ mM}$, and initial $\text{pH} = 9.36 \pm 0.5$).

Clearly, the presence of iron ions (Fe^{2+} and Fe^{3+}) originating from pyrite oxidization by O_2 and H_2O_2 enhanced the formation of $\bullet\text{OH}$, which was responsible for the SBX degradation. However, an excess amount of Fe^{2+} in the Fenton system could react with the generated $\bullet\text{OH}$ through Equation (6), which would consume $\bullet\text{OH}$ and inhibit the oxidative degradation of SBX [44]. Thus, an appropriate concentration of pyrite (0.5 g/L) acted as a catalyst for the Fenton reaction and enhanced the xanthate degradation.



3.1.3. The Effect of Initial SBX Concentration

The effect of initial SBX concentration on the degradation efficiency was further analyzed. As shown in Figure 4, it could be concluded that, generally, the SBX removal rate decreased with the increase in the initial SBX concentration at the same reaction time. It is possible that the oxidation of excess SBX molecules reached saturation and reduced the degradation capacity due to the limited reactive radicals generated by the Fenton reaction in the solution, whereas the initial SBX concentration had little effect on the final removal rate. For instance, even when the SBX concentration was increased to 150 mg/L, the removal rate reached 94.20% after a duration of 85 min. Therefore, considering the effective removal of SBX and reasonable practical application, the selected initial concentration of SBX was 100 mg/L.

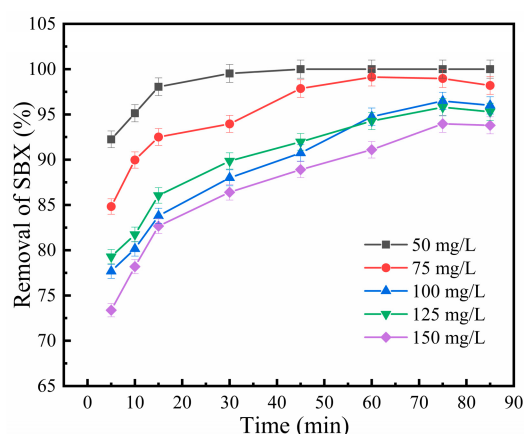


Figure 4. Effect of initial SBX concentration on the removal rate of SBX (conditions: $[\text{H}_2\text{O}_2] = 0.5 \text{ mM}$, $[\text{FeS}_2] = 0.5 \text{ g/L}$, and initial $\text{pH} = 9.36 \pm 0.5$).

3.2. Comparative Experiment Results

Two comparative experiments, (I) a H_2O_2 -alone system and (II) a H_2O_2 - FeS_2 system, were conducted to further verify the specific role of pyrite in degrading SBX, and the results are shown in Figure 5. It can be seen that the SBX removal rate in the H_2O_2 - FeS_2 system reached 96.49% after 75 min under the recommended experimental conditions ($[\text{H}_2\text{O}_2] = 0.5 \text{ mM}$, $[\text{FeS}_2] = 0.5 \text{ g/L}$, $[\text{SBX}] = 100 \text{ mg/L}$, and initial $\text{pH} = 9.36 \pm 0.5$), which was 12.85% higher than the corresponding result in the H_2O_2 -alone system under the same conditions. The results provide strong support for the notion that the H_2O_2 -alone system failed to oxidize SBX completely due to its limited oxidation capacity, while an appropriate concentration of pyrite could act as a catalyst to significantly improve the oxidation capacity of H_2O_2 by establishing a Fenton oxidation system. The utilization of pyrite in combination with H_2O_2 might be an efficient method for the degradation of SBX in flotation tailings wastewater.

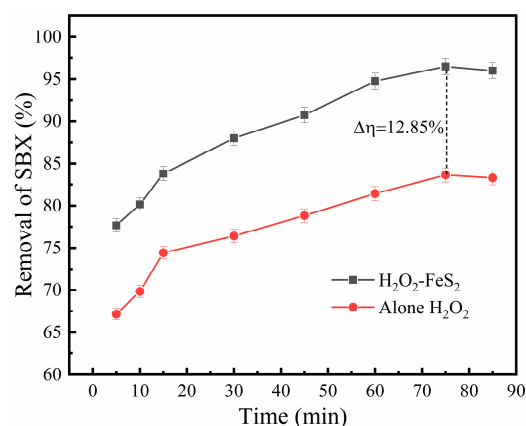


Figure 5. Effects of different oxidation treatments on SBX degradation (conditions: [H₂O₂] = 0.5 mM, [FeS₂] = 0.5 g/L (if present), [SBX] = 100 mg/L, and initial pH = 9.36 ± 0.5).

3.3. SBX Degradation Mechanism in the Pyrite-Catalyzed Fenton System

3.3.1. The Identification of the Reactive Radical

EPR tests were conducted to analyze the generation of free radicals in the reaction system under the recommended experimental conditions. DMPO was used as a trapping agent of hydroxyl radicals because it reacted specifically with hydroxyl radicals and formed DMPO-•OH adducts [25]. In Figure 6a, no significant peaks appear in the spectra of the H₂O₂-alone system, indicating the low generating activity of hydroxyl radicals in this system. In the H₂O₂-FeS₂ system, the adduct is observable as a strong EPR signal with four characteristic peak intensities of 1:2:2:1 for DMPO-•OH. The results confirm that the free radicals produced in the catalytic reaction were •OH. Thus, pyrite could effectively catalyze the decomposition of H₂O₂ and promoted •OH production.

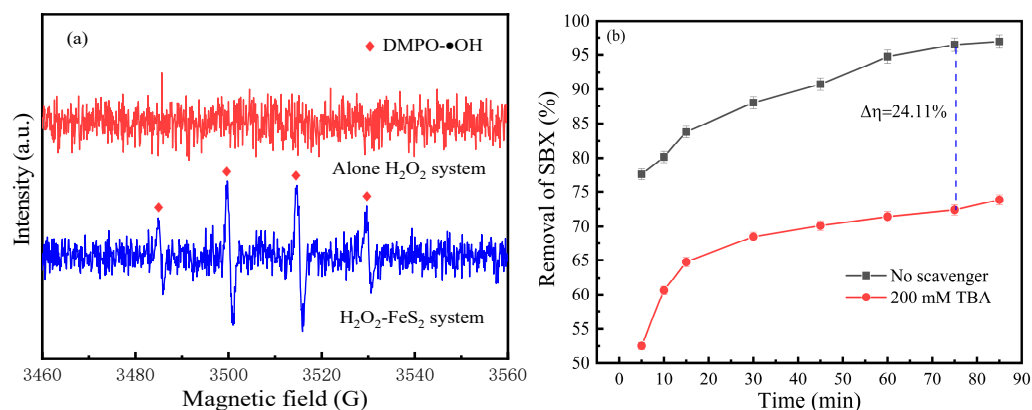


Figure 6. Identification of reactive radical with EPR spectra in the H₂O₂-alone system and H₂O₂-FeS₂ system during the SBX degradation process (a); the role of reactive radical (•OH) in the degradation SBX (b).

Additionally, the role of reactive radicals (•OH) in the degradation SBX was analyzed based on the principle that TBA could capture hydroxyl radicals (•OH), and the results are shown in Figure 6b. The results confirm that the SBX in the H₂O₂-FeS₂ system was almost completely degraded after 75 min of the reaction, while the SBX removal rate was about 72.38% after the addition of 200 mM TBA, which was 24.11% lower than the corresponding result without TBA addition. Notably, the SBX removal rate with TBA addition increased with the increase in the reaction time and presented relatively high levels (>68.49%) when the reaction time was more than 30 min. This phenomenon is mainly attributed to the adoption of SBX onto pyrite's surfaces. This behavior only prompted the SBX transferring from the solution phase to the solid phase, and SBX failed to be mineralized to small

molecules. However, this adoption inevitably caused electron transport and improved the reaction environment, which might have facilitated the interaction between SBX and H_2O_2 . Thus, the reactive radicals ($\bullet\text{OH}$) exerted an important role in the SBX degradation.

3.3.2. UV-Visible Spectrum Analysis Results

The UV full-scan spectrum of the SBX wastewater solution was obtained at a scan range of 200–400 nm and different reaction times (conditions: $[\text{H}_2\text{O}_2] = 0.5 \text{ mM}$, $[\text{FeS}_2] = 0.5 \text{ g/L}$, $[\text{SBX}] = 100 \text{ mg/L}$, and initial $\text{pH} = 9.36 \pm 0.5$) with the aim of analyzing the SBX degradation process. As presented in Figure 7, the obvious absorption peaks located at 301 nm belong to the characteristic absorption peaks of SBX molecules [6]. The peak intensity of the SBX at 301 nm decreased gradually as the reaction time increased from 5 to 85 min. This result indicates that the residual concentration of SBX in the solution gradually decreased with the increasing reaction time. Furthermore, a new peak at 348 nm can be observed in the spectrum at different reaction times, which is assigned to butyl xanthate peroxide (BPX, $\text{C}_4\text{H}_9\text{OCS}_2\text{O}^-$) [45]. The intensity of $\text{C}_4\text{H}_9\text{OCS}_2\text{O}^-$ presented a downtrend as the reaction time extended. This result indicates that SBX was degraded in the H_2O_2 - FeS_2 system, which was accompanied by the generation of an intermediate product (butyl xanthate peroxide). When the reaction exceeded 75 min, the peaks at 301 nm and 348 nm disappeared almost completely. Based on previous literature reports, it is known that SBX might be decomposed into SO_4^{2-} , CO_2 , and H_2O small-molecule substances in the degradation process [13,45].

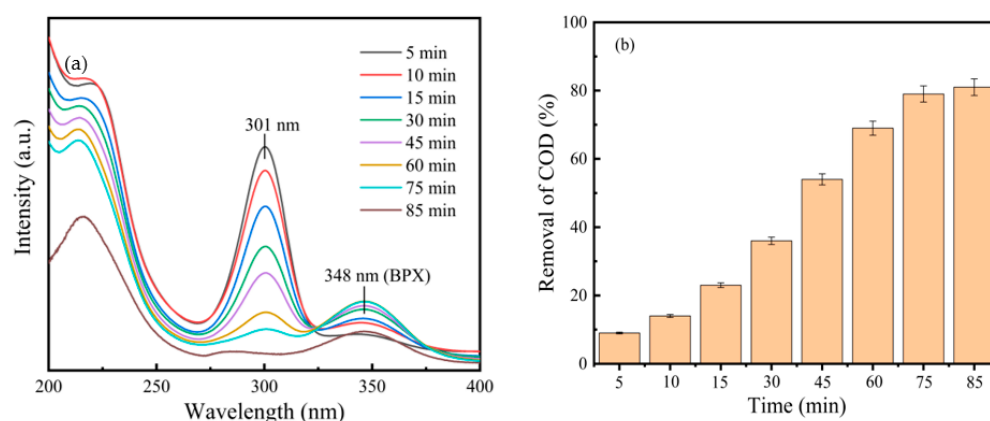


Figure 7. (a) UV-visible spectrum changes in SBX degradation in the pyrite-catalyzed Fenton system with time variations; (b) removal rate of COD at different reaction times (conditions: $[\text{H}_2\text{O}_2] = 0.5 \text{ mM}$, $[\text{FeS}_2] = 0.5 \text{ g/L}$, $[\text{SBX}] = 100 \text{ mg/L}$, and initial $\text{pH} = 9.36 \pm 0.5$).

However, the determination of SBX contaminants at 301 nm using UV-vis spectroscopy may have been interfered with by iron ions. To further analyze the degradation performance of SBX in the H_2O_2 - FeS_2 system, the COD of the solution samples was determined at different reaction times. As shown in Figure 7b, the COD removal rate increased with the increase in the reaction time within 75 min. When the reaction was carried out at 75 min, the COD removal rate reached 79%, which was possibly due to the further decomposition of the formed intermediates (i.e., $\text{C}_2\text{H}_5\text{OCS}_2\text{O}^-$) into small inorganic molecules. When the reaction time was further extended, the COD removal rate did not change significantly, indicating that SBX and its intermediates were almost completely decomposed into small molecules such as SO_4^{2-} , CO_2 , and H_2O . This is in agreement with the results of the UV-visible analysis.

3.3.3. Solution pH and Iron Concentration Analysis

The solution pH and concentration variation in the iron ions in the pyrite-catalyzed Fenton system are shown in Figure 8. As shown in Figure 8a, the solution pH decreased gradually as the reaction time extended from 5 to 85 min. Specifically, the initial pH of 9.36 ± 0.5 decreased to a final pH of 7.4 ± 0.5 . This was due to the fact that the SBX was

decomposed into CO_2 , H_2O , and SO_4^{2-} . The concentration of total dissolved Fe exhibited an obvious increasing trend (Figure 8b). Meanwhile, the aqueous Fe^{2+} concentration remained at a low concentration without significant variation instead of running out, which ensured that the reaction proceeded continuously, indicating that aqueous Fe^{2+} was constantly released from the pyrite surface and that the Fe^{3+} recycle existed, as shown in Equation (5). Additionally, it could be concluded that the Fe^{3+} concentrations in the solution increased significantly because the aqueous Fe^{2+} generated from the pyrite surface was soon oxidized to Fe^{3+} used for the formation of $\bullet\text{OH}$ in the pyrite Fenton reaction. This result indicates that pyrite could significantly enhance the reactivity of a H_2O_2 system.

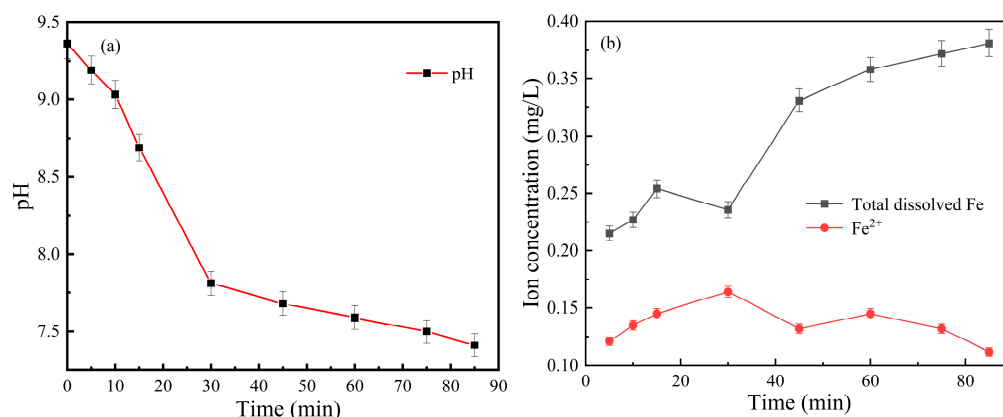


Figure 8. Effects of reaction time on the solution pH (a) and on the concentrations of Fe^{2+} and total dissolved Fe (b) along with the degradation of SBX in the pyrite-catalyzed Fenton system (conditions: $[\text{H}_2\text{O}_2] = 0.5 \text{ mM}$, $[\text{FeS}_2] = 0.5 \text{ g/L}$, $[\text{SBX}] = 100 \text{ mg/L}$, and initial $\text{pH} = 9.36 \pm 0.5$).

Along with the aforementioned results and discussion, we propose a reaction mechanism for SBX degradation via a pyrite-catalyzed Fenton system. As shown in Figure 9, the H_2O_2 adsorbed onto the pyrite surface and reacted with Fe^{2+} , triggering the formation of reactive radicals ($\bullet\text{OH}$) and Fe^{3+} . The $\bullet\text{OH}$ attacked the SBX that adsorbed on the pyrite surface or existed in the solution and promoted the transformation of the SBX anion ($\text{C}_4\text{H}_9\text{OCS}_2^-$) into the intermediate butyl xanthate peroxide (BPX, $\text{C}_4\text{H}_9\text{OCS}_2\text{O}^-$). Finally, BPX intermediates were further oxidized to smaller products such as SO_4^{2-} and the inorganic substances CO_2 and H_2O . Given the above results, the natural pyrite acted as a catalyst for the heterogeneous Fenton reaction and enhanced SBX degradation in the flotation tailings wastewater considerably.

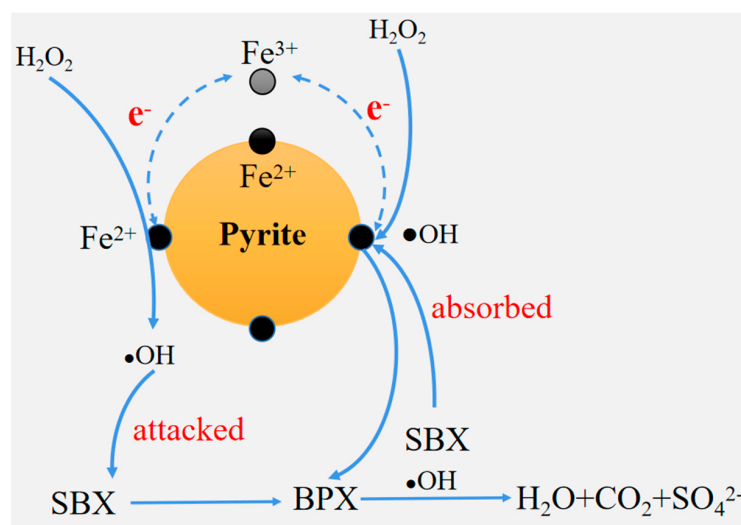


Figure 9. Proposed reaction mechanism for SBX degradation via pyrite-catalyzed Fenton system.

4. Conclusions

The pyrite-catalyzed Fenton system exhibited excellent degradation efficiency for SBX, and under the same conditions, this system degraded SBX more efficiently than the H_2O_2 system. An appropriate concentration of pyrite acted as a catalyst to significantly improve the oxidation capacity of H_2O_2 by establishing a Fenton oxidation system. The concentration of total dissolved Fe exhibited an obvious increasing trend in the system and the aqueous Fe^{2+} concentration remained at a low concentration, indicating that aqueous Fe^{2+} was constantly released from the pyrite surface. Additionally, the results of EPR and quenching measurements suggested that hydroxyl radicals were the main active species in the H_2O_2 - FeS_2 system for the degradation of SBX. A possible reaction mechanism was proposed. H_2O_2 adsorbed onto the pyrite surface and reacted with Fe^{2+} , triggering the formation of reactive radicals ($\bullet\text{OH}$) and Fe^{3+} . The $\bullet\text{OH}$ most likely attacked the SBX that adsorbed on the pyrite surface or existed in the solution and promoted the transformation of the SBX anion ($\text{C}_4\text{H}_9\text{OCS}_2^-$) into the intermediate butyl xanthate peroxide (BPX, $\text{C}_4\text{H}_9\text{OCS}_2\text{O}^-$). Finally, BPX intermediates were likely further oxidized to smaller products such as SO_4^{2-} , CO_2 , and H_2O under the ongoing attack of $\bullet\text{OH}$.

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