Degradation of ethylthionocarbamate by pyrite-activated persulfate

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ABSTRACT

Ethylthionocarbamate (ETC) is the most widely used collector in the flotation of sulfide minerals. However, it is known to cause serious pollution to soil and groundwater systems. Pyrite is the most abundant iron sulfide mineral in the Earth's crust, and can effectively activate persulfate (PS) to produce $SO_4^{-}\cdot$. Compared with heavy metals, natural iron-containing minerals are relatively non-toxic, inexpensive, and environment-friendly PS activators that can be used for removing refractory organic pollutants. In this study, batch experiments were conducted to investigate ETC degradation by pyrite-activated PS. The activation mechanism, and the effect of various factors, namely, initial pH, pyrite dosage, PS concentration, and coexisting ions, were examined. ETC was efficiently degraded by pyrite-activated PS, and its degradation increased with increasing pyrite dosage and PS concentration, and decreasing pH. Moreover, the presence of Mn^{2+}, Cu^{2+}, CO_3^{2-}, PO_4^{3-}, and HCO_3^{-} had a significant inhibitory effect on ETC degradation, in the following order: $PO_4^{3-} > HCO_3^{-} > CO_3^{2-} > Mn^{2+} > Cu^{2+}$. These findings indicate that the PS-pyrite system provides a new method for ETC removal from flotation wastewater.
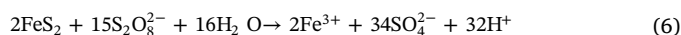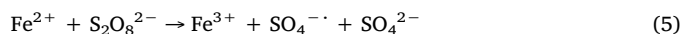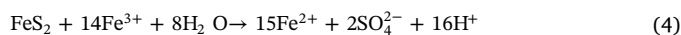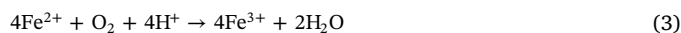
1. Introduction

Ethylthionocarbamate (ETC) is widely used as a flotation collector for sulfide minerals (Bulatovic, 2007). However, because of its high toxicity and difficult biodegradation, the leaching of flotation wastewater from tailing dams, especially in to the soil and groundwater, is a major environmental problem (Cheng et al., 2012; Molina et al., 2013; Chen et al., 2011).

Currently, conventional wastewater treatments, such as activated carbon adsorption and chemical precipitation, are used to remove collectors from flotation wastewaters. However, these methods have some limitations, e.g. in meeting water quality standards for safe discharge (Fu et al., 2015). Thus, a highly efficient treatment of flotation wastewater is highly desirable.
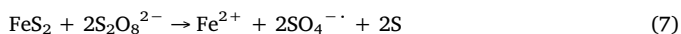
Advanced oxidation processes (AOPs) have become a promising technology for the degradation of refractory organic pollutants in wastewater. In particular, persulfate (PS) has attracted much interest as a strong oxidizing agent due to its many advantages, such as high redox potential ($E_0 = 2.01$ V) (Zhang et al., 2017), non-selectivity over a wide pH range, relative stability, easy storage and transportation, and low cost (Hussain et al., 2012; Rao et al., 2014). PS can be activated by heat (Zrinyi and Pham, 2017), UV light (Yang et al., 2010), transition metals (such as Fe^{2+}, Cu^{2+}, Co^{2+}, and Ag^+) (Lei et al., 2015), activated carbon (Matzek and Carter, 2016), and quinones (Fang et al., 2013).

Although PS activation by transitions metal has the advantages of high efficiency and low energy consumption, iron-containing compounds have recently attracted particular attention because of their efficiency, nontoxicity, low cost, and natural abundance. However, in homogeneous processes, sulfate radicals ($SO_4^{-}\cdot$) ($E_0 = 2.6$ V) are rapidly scavenged by excess Fe^{2+} (Eq. (1)), resulting in reduced oxidation of pollutants (Liang et al.,2004). Hence, recent research efforts focused on heterogeneous AOPs using PS (Cai et al., 2014). However, most of these studies were limited to synthetic iron composites, whereas systematic studies of natural iron-containing minerals are scarce. Pyrite is the most abundant iron sulfide mineral in the Earth's crust, and because of its high iron content, can activate PS for the in situ degradation of organic pollutants (Eqs. (2)–(7)) (Zhang et al., 2017).

$$Fe^{2+} + SO_4^{-}\cdot \rightarrow Fe^{3+} + SO_4^{2-} \tag{1}$$

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \tag{2}$$

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \tag{3}$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \tag{4}$$

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{-}\cdot + SO_4^{2-} \tag{5}$$

$$2FeS_2 + 15S_2O_8^{2-} + 16H_2O \rightarrow 2Fe^{3+} + 34SO_4^{2-} + 32H^+ \tag{6}$$

$$FeS_2 + 2S_2O_8{}^{2-} \rightarrow Fe^{2+} + 2SO_4{}^{-\cdot} + 2S \qquad (7)$$

To the best of our knowledge, very few reactions between ETC and pyrite -activated PS have been reported. In this study, the PS activation mechanism by pyrite in the ETC degradation process and the effect of various factors, namely, pyrite dosage, initial pH, PS concentration and coexisting ions, were investigated.

2. Materials and methods

2.1. Materials

ETC was purchased from Zhuzhou Mineral Processing Reagent Plant (Zhuzhou, China). Pyrite samples were collected from a mining in Hunan province, China, ground with milled by a hammermill, and sieved to obtain fine particles with a diameter of < 150 μm. Concentrated sulfuric acid, sodium hydroxide, sodium persulfate, sodium bicarbonate, potassium iodide, methanol, and *tert*-butyl alcohol (TBA) were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals were used without further purification, and solutions were prepared with deionized water obtained from a Milli-Q system (Millipore, USA).

2.2. Experimental setup

All glassware was soaked with 5N HNO$_3$, thoroughly rinsed with deionized water, and baked at 105 °C for 2 h prior to use. All experiments carried out in 250-mL flasks containing 150 mL ETC solution with a concentration of 30 mg/L. The flasks were kept in a thermostated water bath at 150 rpm and 28 °C under ambient O$_2$ conditions in the absence of light. The initial pH values were adjusted with 0.05 M NaOH or H$_2$SO$_4$ solution. The reaction was initiated by adding an appropriate amount of sodium persulfate and pyrite. At regular time intervals, 10 mL samples were withdrawn from each flask and immediately passed through 0.45 μm membrane filters. After filtration, 0.5 mL of methanol was added to each sample, and the mixture was vigorously shaken for 2 min using a vortex shaker to quench the reaction before analysis. All experiments were performed in triplicate.

Various factors affecting ETC degradation, namely, pyrite dosages, PS concentrations, pH, and coexisting ions, were examined. At first, the reaction was investigated at five pH values (3, 5, 7, 9, and 11), and pH 5 was used in the following experiments. Various pyrite dosages, namely, 0.1, 0.3, 0.5, 0.7, and 1.0 g/L, and PS concentrations, namely, 0.012, 0.024, 0.048, 0.072, 0.096, and 0.12 g/L, were examined. The effect of coexisting ions was evaluated by adding 10 mM NH$_4{}^+$, Mn^{2+}, Cu^{2+}, Mg^{2+}, Al^{3+}, NO$_3{}^-$, CO$_3{}^{2-}$, PO$_4{}^{3-}$, Cl$^-$, and HCO$_3{}^-$ to the background solutions.

2.3. Analytical methods

A pH meter (Hach, USA) was used for pH measurements. ETC concentrations were determined using a UV–vis spectrophotometer (Shimadzu, Japan) at 241 nm, and PS concentrations were determined by iodometric titration with sodium thiosulfate (Liang et al., 2008). Fe^{2+} concentrations were measured by the 1,10-phenanthroline method. The total dissolved iron was determined by inductively coupled plasma mass spectrometry (NexION 300). The crystal structure of pyrite was characterized by X-ray diffraction (XRD) using a Bruker D8 Advance instrument (Cu Kα radiation).

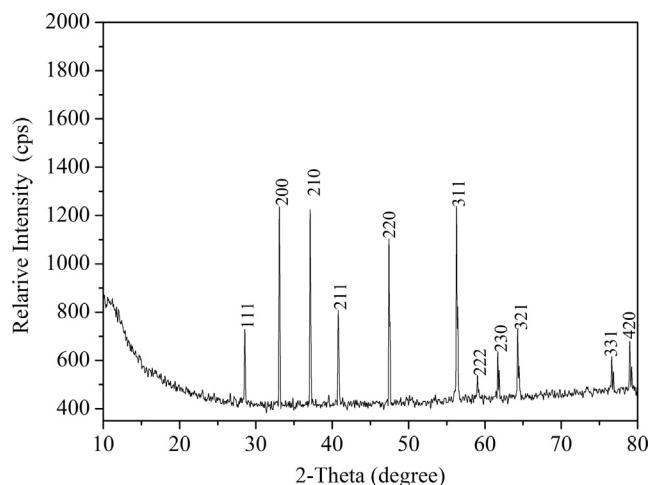## 3. Results and discussion

3.1. Characterization of pyrite

The chemical composition of pyrite is listed in Table 1. As can be

Table 1
The chemical composition of pyrite.

Composition	Sample ratio (%)
Fe	45.94
S	52.963
Al$_2$O$_3$	0.085
SiO$_2$	0.766
K$_2$O	0.022
CaO	0.091
Cr$_2$O$_3$	0.07
As$_2$O$_3$	0.063

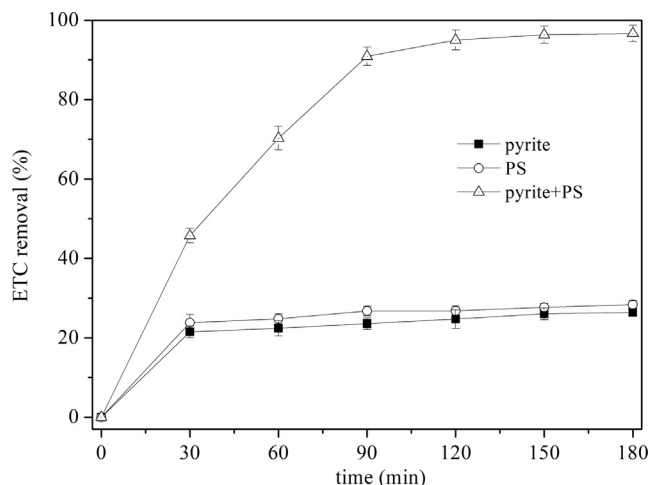

Fig. 1. XRD pattern of pyrite.

seen from Fig. 1, the XRD pattern shows only the diffraction peaks of the FeS$_2$ phase, indicating a high pyrite of pyrite.

3.2. ETC degradation by pyrite, PS, and PS-pyrite systems

ETC removal by pyrite, PS, and PS-pyrite was investigated, and the results are shown in Fig. 2. After180 min, only 26.39% ETC was removed by the pyrite-only system mainly due to the adsorption of ETC on the pyrite surface. A similar result was obtained for the PS-only system, with about 28.35% of ETC removed in the same time. Notably, pronounced ETC degradation was observed when 1.0 g/L pyrite was added to the PS solution, achieving 96.64% removal at 180 min. These results demonstrate that pyrite could activate PS to enhance ETC degradation.

Fig. 2. ETC degradation by pyrite, PS, and PS-pyrite systems.