



Mechanisms of hydroxyl radicals production from pyrite oxidation by hydrogen peroxide: Surface versus aqueous reactions

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Received 8 February 2018; accepted in revised form 10 July 2018; Available online 19 July 2018

Abstract

Pyrite oxidation by hydrogen peroxide (H_2O_2) occurs in both natural and engineered systems. Hydroxyl radical ($\cdot\text{OH}$) is a key reactive intermediate for pyrite and coexisting substances oxidation. In acidic H_2O_2 /pyrite systems, H_2O_2 decomposition by aqueous Fe^{2+} is documented to predominate for $\cdot\text{OH}$ production, whereas here we show that H_2O_2 decomposition by surface $\text{Fe}(\text{II})$ sites contributes considerably to $\cdot\text{OH}$ production under certain conditions. Pyrite oxidation by H_2O_2 under anoxic conditions was performed under different conditions (2–12 g/L pyrite, 0.025–1 mM H_2O_2 and pH 2–4), and $\cdot\text{OH}$ and aqueous $\text{Fe}^{2+}/\text{Fe}^{3+}$ production as well as H_2O_2 consumption were measured during the oxidation. In order to evaluate the contribution of surface reaction to $\cdot\text{OH}$ production, 1 mM 2, 2'-bipyridine (BPY) was added to inhibit H_2O_2 decomposition by aqueous Fe^{2+} . The rate constants of $\cdot\text{OH}$ production decreased by 44.4–65.6% with addition of 1 mM BPY, which suggests that both surface and aqueous reactions contributed to $\cdot\text{OH}$ production. Regarding the surface reaction, density functional theory (DFT) calculation reveals that H_2O_2 was adsorbed onto the $\text{Fe}(\text{II})$ sites on pyrite surface and transformed to surface adsorbed $\cdot\text{OH}$ which desorbed subsequently into the aqueous solution. On the basis of mechanistic understanding, a kinetic model was developed to assess the relative contributions of surface and aqueous reactions to $\cdot\text{OH}$ production. The relative contribution of surface reaction is dependent on the ratio of pyrite surface concentration to aqueous Fe^{2+} concentration, which decreases with the progress of pyrite oxidation due to the increase in aqueous Fe^{2+} . When the ratio is higher than the threshold value of $1.6 \times 10^3 \text{ m}^2/\text{mM}$, surface reaction becomes predominant for $\cdot\text{OH}$ production. Typical systems necessitating consideration of surface reaction involve pyritic rocks and shale leaching and pollutants treatment by H_2O_2 /pyrite. The mechanisms unraveled in this study supplement the fundamental of $\cdot\text{OH}$ production from pyrite oxidation by both H_2O_2 and O_2 in natural and engineered systems.

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Keywords: Hydroxyl radical; Pyrite; Oxidation; Surface; Hydrogen peroxide

1. INTRODUCTION

Pyrite oxidation plays an important role in the biogeochemical cycling of iron (Fe) and sulfur (S) throughout

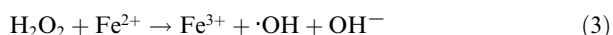
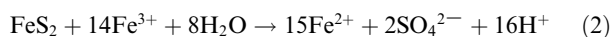
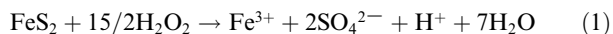
the Earth's geological history (Moses and Herman, 1991; Schippers and Jørgensen, 2002). Oxygen (O_2) and ferric iron (Fe^{3+}) are the common oxidants for pyrite in supergene environments (Moses and Herman, 1991; Williamson and Rimstidt, 1994). Hydrogen peroxide (H_2O_2) is found to oxidize pyrite under anoxic subsurface environments associated with uranium deposits and under

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pyrite-bearing oxic systems (Lefticariu et al., 2006; Lefticariu et al., 2007; Lefticariu et al., 2010; Schoonen et al., 2010; Kaur and Schoonen, 2017). H₂O₂ is also widely used for pyritic rocks and shale leaching (McKibben and Barnes, 1986; Dimitrijevic et al., 1996; Antonijević et al., 1997; Chandra and Gerson, 2011). Given the importance of pyrite oxidation by H₂O₂ in geological processes and engineered systems, many studies have been devoted to exploring the mechanisms and kinetics under different conditions (McKibben and Barnes, 1986; Dimitrijevic et al., 1996; Antonijević et al., 1997; Lefticariu et al., 2006; Chirita, 2007; Lefticariu et al., 2007; Chandra and Gerson, 2011; Sun et al., 2015). Schoonen's group first documented that hydroxyl radicals (·OH), a strongly reactive oxidant (standard reduction potential: 2.8 V, Wardman, 1989), was produced in H₂O₂/pyrite systems and caused oxidative damage to adenine and nucleic acid (Cohn et al., 2006; Cohn et al., 2009; Cohn et al., 2010; Che et al., 2011; Fisher et al., 2012). Recent studies substantiate that the ·OH produced in H₂O₂/pyrite systems can oxidize pollutants (Bae et al., 2013; Zhang et al., 2014; Ammar et al., 2015; Wu et al., 2015). Therefore, it is essential to unravel the mechanisms of ·OH production from pyrite oxidation by H₂O₂.

For pyrite oxidation by H₂O₂, previous studies claimed that H₂O₂ decomposition by aqueous Fe²⁺ through the Fenton mechanism was mainly responsible for ·OH production (Cohn et al., 2006; Lefticariu et al., 2006; Lefticariu et al., 2007; Fisher et al., 2012; Bae et al., 2013; Zhang et al., 2014; Wu et al., 2015). Under acidic conditions, pyrite is firstly oxidized by H₂O₂ producing Fe³⁺ and sulfate (SO₄²⁻) (Eq. (1), McKibben and Barnes, 1986). Fe³⁺ is reduced to Fe²⁺ by pyrite (Eq. (2), Moses and Herman, 1991), and Fe²⁺ further reacts with H₂O₂ producing ·OH (Eq. (3), Lefticariu et al., 2006). When exposed to air, pyrite oxidation by O₂ may produce Fe²⁺ (McKibben and Barnes, 1986; Schoonen et al., 2010; Zhang et al., 2014), and Fe²⁺ regeneration is regarded as the critical step for ·OH production. For instance, Wu et al. (2015) noted that the addition of Fe³⁺ enhanced chloramphenicol oxidation due to the increase in Fe²⁺ generation from Fe³⁺ reduction by pyrite. In addition to the oxidative dissolution of pyrite, non-oxidative dissolution can also produce Fe²⁺ (Kamei and Ohmoto, 2000; Demoisson et al., 2005; Rickard and Luther, 2007; Graham and Bouwer, 2012), which likely contributes to ·OH production.



According to Eqs. (1)–(3), both pyrite surface and aqueous Fe²⁺ contribute putatively to H₂O₂ decomposition. It has been documented that H₂O₂ can be decomposed to ·OH by surface Fe(II) on Fe(III) minerals under acidic conditions (Huang et al., 2016; Hou et al., 2017). Because of the abundance of Fe(II) sites on pyrite surface, it is likely that the surface reaction (Eq. (1)) contributes to ·OH production besides the aqueous reaction (Eq. (3)). The surface reaction between H₂O₂ and pyrite surface was proposed (Schoonen

et al., 2010; Zhang et al., 2016), but it was not justified for ·OH production. H₂O oxidation by surface sulfur-defects has been confirmed for ·OH production (Borda et al., 2003; Zhang et al., 2016). As the surface and aqueous reactions are respectively dependent on pyrite surface and aqueous Fe²⁺ concentrations, it is rational to conjecture that the contribution of surface reaction to ·OH production varies with reaction time and conditions.

Therefore, the objectives of this study are to ascertain (1) whether and how the surface reaction contributes to ·OH production, and (2) to what extent each pathway contributes to ·OH production and how the contributions vary with reaction conditions in acidic H₂O₂/pyrite systems. Pyrite oxidation by H₂O₂ under anoxic conditions was performed under different conditions (2–12 g/L pyrite, 0.025–1 mM H₂O₂ and pH 2–4). Sodium benzoate (BA, $k_{\text{BA},\cdot\text{OH}} = 4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, Buxton et al. (1988)) was added as a probe compound to trap the ·OH that was produced from pyrite oxidation by H₂O₂ (Mopper and Zhou, 1990; Joo et al., 2005; Tong et al., 2016; Zhou et al., 2017). To quantify the ·OH that was produced from surface reaction, 2, 2'-bipyridine (BPY) was added to chelate the aqueous Fe²⁺, thus inhibiting H₂O₂ decomposition by aqueous Fe²⁺ (Katsoyiannis et al., 2008). The changes of Fe, O and S speciation during pyrite oxidation were characterized by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). Mechanism of ·OH production from surface reaction was evaluated by density functional theory (DFT). A kinetic model was ultimately developed to assess the relative contributions of each pathway for ·OH production.

2. MATERIALS AND METHODS

2.1. Chemicals

BA (99.5%), *p*-hydroxybenzoic acid (*p*-HBA, 99%), H₂O₂ (30%) and BPY (99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd, China. All the other chemicals are of above analytical grade. Deionized (DI) water (18.2 MΩ cm) from a Heal Force NW ultra-pure water system was used in all the experiments. The presence of reactive oxygen species (·OH, ·O₂⁻ and H₂O₂) in the DI water has been proven to be negligible (Zhang and Yuan, 2017).

Natural pyrite was received from Shizishan mine in Anhui province, China. It was crushed and sieved to <74 μm. Pyrite particles were washed with 1 M HCl for 60 min to remove the oxidized layers on the surface. Subsequently, pyrite suspension was vacuum-filtered and washed with DI water until the supernatant pH was 6–7. Finally, it was dried in a freezer dryer (Lab-1A-50E, Biocool, China) and stored in an anoxic glove box (Mikrouna, China) filled with Ar (99.999%). The mass percentages of Fe, S, Si, Ca and Zn were measured to be 45.1%, 51%, 1.2%, 1.83% and 0.18%, respectively (Zhang et al., 2016). The specific surface area of pyrite was measured to be 3.46 m²/g through multipoint (54 points) BET (Brunauer, Emmett and Teller) analysis with N₂ adsorption at 77 K on a Micromeritics surface area analyzer (ASAP-2020).

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