

Pyrite-enhanced degradation of chloramphenicol by low concentrations of H₂O₂

Deli Wu, Yanxia Liu, Zhiyong Zhang, Luming Ma and Yalei Zhang

ABSTRACT

A pyrite-catalyzed reaction was used to degrade chloramphenicol. Chloramphenicol could be almost 100% removed within 60 minutes when 1 mM H₂O₂ and 0.1 g/L pyrite were added at an initial pH = 3. During oxidation, intermediates such as nitrobenzaldehyde and dichloroacetamide were identified by gas chromatography/mass spectrometry (GC/MS). The •OH was identified by electron spin-resonance spectroscopy. Pyrite was digested to determine elements by ICP (inductive coupled plasma emission spectrometer). To understand the reaction mechanism and the role of natural pyrite in these processes, techniques including scanning electron microscopy and energy dispersive spectrometry were employed to characterize the solid sample. The results explain that pyrite acts as a 'bond' between Fe³⁺ and H₂O₂, and this pathway continues to form •OH and inhibit the quenching reaction. Therefore, pyrite-catalyzed reactions would proceed even in low concentrations of H₂O₂.

Key words | Fenton-like, H₂O₂, heterogeneous, mechanism, pyrite

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INTRODUCTION

Chloramphenicol (CAP) is a prototypical broad band spectrum antibiotic, which is effective against a wide variety of gram-positive and gram-negative bacteria (Daughton & Ternes 2000). In the West, CAP is widely used in topical preparations for the treatment of bacterial conjunctivitis, such as ointments and eye drops. In developing countries, CAP is widely used because it is inexpensive and readily available (Ronning *et al.* 2006). As shown in Figure S1 (available online at <http://www.iwaponline.com/wst/072/202.pdf>), nitro, phenyl, and chlorine groups exist in the CAP structure. CAP may cause disease in hemopoietic systems and the digestive system according to recent research (Festing *et al.* 2001). Furthermore, CAP entering the environment with inefficient treatment could cause ecological risk and threaten the health of animals and humans (Hernando *et al.* 2006). Thus, it is important to explore suitable processes to treat water and wastewater containing CAP.

Advanced oxidation processes are an ideal method to treat refractory pollutants. Among the advanced oxidation processes, the Fenton reactions have been widely investigated due to high oxidation capacity. However, the traditional homogenous Fenton reactions have disadvantages, including the production of ferric hydroxide sludge and pH limitations (Che & Lee 2011; Huang *et al.* 2012). To overcome these limitations, heterogeneous Fenton-like

processes have attracted more attention recently. Photocatalytic degradation of CAP has been reported (Chatzidakis *et al.* 2008; Zhang *et al.* 2010), where TiO₂ and ZnO were employed as catalysts. Chlorine could be eliminated completely under appropriate treatment conditions, while the nitrogen in CAP was recovered as nitrate and ammonium ions. Glucose was employed as an intracellular electron donor, and a biocathode served as the extracellular electron donor. CAP removal efficiency reached 96% with a bioelectrochemical system (Liang *et al.* 2013; Sun *et al.* 2013). Although the degradation of CAP has been evaluated with various Fenton or Fenton-like methodologies, pyrite-catalyzed H₂O₂ in the degradation of CAP has thus far rarely been reported.

Pyrite is a natural mineral, which has been successfully used as a Fenton reaction material to degrade organic pollutants such as methylene blue, nitrobenzene, and diclofenac (Benetoli *et al.* 2012; Bae *et al.* 2013; Zhang *et al.* 2014). These results provide a promising insight into the application of pyrite as a catalyst in the CAP Fenton reaction. Although much work has been done in pyrite-catalyzed reactions, a great deal of pyrite and H₂O₂ was consumed. The reaction mechanism between pyrite and H₂O₂ in low H₂O₂ concentrations is not clear. Furthermore, the CAP decomposition pathway has not been studied in detail.

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This paper investigates the reaction mechanism of pyrite-enhanced degradation of CAP at low H₂O₂ concentrations, as well as the pathway of CAP decomposition. To propose a general reaction pathway for CAP in a pyrite–H₂O₂ system, experiments have clarified the effect of several experimental parameters on CAP degradation, formation of intermediates, and their evolution. We close with a discussion of the role of pyrite in the reaction.

EXPERIMENTAL

Chemicals and materials

Hydrogen peroxide (30%, w/w), sulfuric acid, and sodium hydroxide of analytical grade were supplied by Chemicals Corporation (Shanghai, China). Ethyl acetate of HPLC grade was purchased from ANPEL Scientific Instrument Co., Ltd (Shanghai, China). CAP of HPLC grade was obtained from J&K Chemical Co., Ltd (Beijing, China). All solutions were prepared with 18 MΩ Milli-Q water from a Millipore system (Bedford, MA, USA). The natural pyrite sample was obtained from LvLing Chemical Industry Group Co., Ltd (Jiangsu, China).

Oxidation procedure

Experiments were performed at laboratory-scale and room temperature (25 ± 2 °C). In all cases, 200 mL of 50 mg/L CAP solution containing the appropriate quantity of catalyst powder and H₂O₂ were magnetically stirred to keep the pyrite suspended. At specific time intervals, 1 mL samples were withdrawn and 10 μL methanol was added to terminate the reaction. The samples were filtered with 0.45 μm filters to remove pyrite particles (ANPEL Scientific Instrument Co., Ltd, Shanghai).

Analytical procedures

The CAP was measured with an Agilent 1,260 liquid chromatography system (Agilent Technologies, Santa Clara, CA, USA) equipped with a quaternary solvent delivery system, an auto sampler, and a DAD detector. Elution was performed on an Agilent Eclipse XDB C18 column (5 μm; 4.6 × 250 mm; Agilent Technologies, Santa Clara, CA, USA) with methanol/H₂O (50:50; v/v) as the mobile phase at a flow rate of 0.6 mL min⁻¹ with UV detection at 270 nm.

The determination of chloride ions and sulfate ions was performed by an ion chromatography (IC) (ICS-900, Dionex,

Sunnyvale, CA, USA) equipped with an IonPac AG23 guard column (4 × 50 mm ID; Dionex, Sunnyvale, CA, USA) and an anion AS23 (4 × 250 mm ID; Dionex, Sunnyvale, CA, USA) analytical column with 4.5 mM Na₂CO₃/1 mM NaHCO₃ as the eluent at a flow rate of 1.0 mL·min⁻¹ as the mobile phase.

To identify the products during CAP transformation, gas chromatography/mass spectrometry (GC/MS) tests were performed. Chromatography was performed with a Trace DSQII (Thermo Fisher, Santa Clara, CA, USA) equipped with an MS detector. Samples were separated and evaluated with a non-polar HP-5 column (J&W Scientific, Folsom, CA, USA; 30 m × 0.25 mm ID × 0.25 mm film thickness). The oven temperature was programmed from 50 to 280 °C at 25 °C/min with a 1 minute initial hold and a 5 minute final hold. The source was kept at 230 °C, the transfer line was maintained at 250 °C, and the injector at 250 °C. Electron impact ionisation in positive ion mode was used (70 eV). Helium was the carrier gas at 1.0 mL/min. The injections were splitless.

Pyrite was placed in a Teflon crucible and digested with a mixture of *aqua regia* and hydrofluoric acid. It was finally dissolved in 1% nitric acid. Combustion residues were digested on an as-received basis. The concentration of elements was determined by inductively coupled atomic emission spectrometry (ICP-AES).

The electron spin resonance (ESR) spectroscopy experiments (Bruker EMX-8/2.7, Bruker Corporation, Bremen, Germany) verified the existence of •OH in the system. They were conducted in a series of polyethylene centrifuge tubes equipped with an XW-80A vortex mixer. As the spin trapped the reagent, the concentration of DMPO was 100 μM. Then, 25 g/L of pyrite powder was added into a 7 mL polyethylene centrifuge tube filled with 20 μL DMPO and 100 mM H₂O₂. The reaction continued for 2 minutes to trap the •OH. Then, the mixed solution was taken out. When the sample was filled to about two-thirds volume of the glass capillary, it was set to an ESR spectrometer to acquire DMPO-OH adduct spectra. The filling step was finished within 1.5 minutes.

RESULTS AND DISCUSSION

Degradation of CAP by pyrite-catalyzed H₂O₂

Influence of the H₂O₂ dosage

As shown in Figure 1(a), 100 mg/L pyrite was added to 200 mL solution to remove 50 mg/L CAP by the above

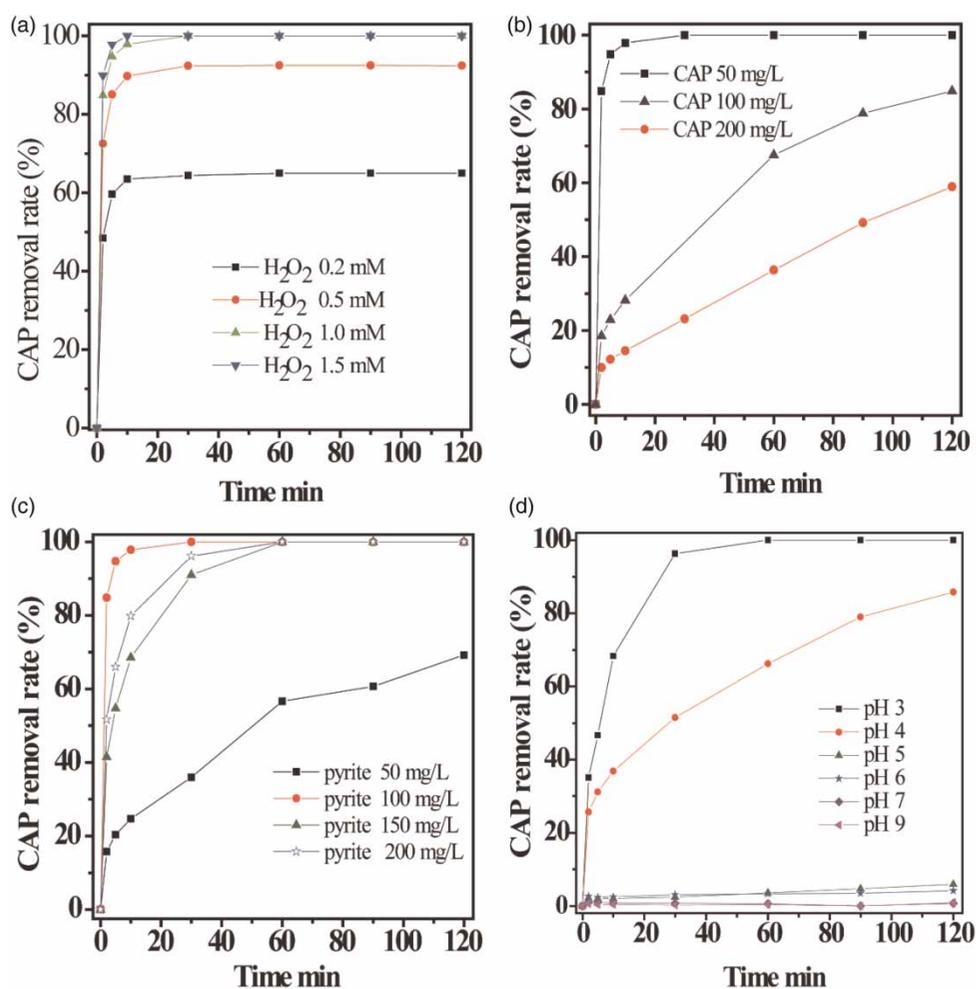


Figure 1 | Effect of H₂O₂ dosage (a), effect of CAP concentration (b), effect of pyrite dosage (c), and effect of initial pH (d).

procedures. The initial pH of the CAP wastewater was unadjusted as it was 3 after pyrite and H₂O₂ were added, whatever the dosages. Pyrite catalyzed by H₂O₂ showed good efficiency in removing CAP because the CAP decomposed completely in 30 minutes with 1 mM H₂O₂. In addition, an increase of reaction time from 30 to 120 minutes caused only a slight enhancement of CAP removal efficiency. We observed 65% CAP decomposition with 1 mM H₂O₂ in 30 minutes. The concentration of SO₄²⁻, Cl⁻, and NO₃⁻ was detected after reaction under each condition. As the concentration of H₂O₂ increased, the concentration of Cl⁻ and NO₃⁻ increased, but SO₄²⁻ did not increase. As SO₄²⁻ can only be produced by pyrite in this reaction, it implies that pyrite was consumed during the reaction because pyrite participates in the heterogeneous oxidation process; however, the loss of pyrite was always around 2.5%. The majority of H₂O₂ participates in the degradation of CAP. The concentration

of H₂O₂ decreased from 1 mM to 0.382 mM after a reaction of 2 hours.

Influence of the CAP concentration

As shown in Figure 1(b), 100 mg/L pyrite and 1 mM H₂O₂ were added to the reaction system at the lowest CAP initial concentration (50 mg/L); the degradation rate of CAP was rapid. The highest removal efficiency of CAP was more than 95% after 10 minutes, whereas the degradation rate of CAP gradually slowed with an increasing initial concentration of CAP. Nearly 60% of CAP was removed after 2 hours when the initial concentration of CAP was 200 mg/L. No equilibrium was achieved even after 2 hours. These results suggest that pyrite-catalyzed systems have satisfied oxidation capability. It also demonstrates that pyrite-catalyzed reactions have good H₂O₂ utilization efficiency; H₂O₂ can be continuously catalyzed by pyrite to degrade

CAP. These impressive results are attributed to special reaction pathways where FeS_2 could react with Fe^{3+} to produce Fe^{2+} (Cohn *et al.* 2004), reducing the consumption of H_2O_2 and S_2^{2-} could donate electrons accelerating the degradation process.

Influence of the pyrite dosage

The relationship between CAP removal efficiency and the initial pyrite dosage is shown in Figure 1(c). The same efficiency has been obtained for three doses of pyrite (100, 150, and 200 mg/L) with 1 mM H_2O_2 . At the lowest dose of this catalyst (50 mg/L), CAP removal occurs at the lowest rate. Pyrite catalyzes H_2O_2 with various pyrite dosages corresponding to a pseudo-first-order kinetic pathway as shown in Table S1 (available online at <http://www.iwaponline.com/wst/072/202.pdf>). The pseudo-first-order kinetic rate constant for decomposition of CAP increased from 0.93 to 8.87 ($10^{-2}/\text{min}$) as pyrite dosage increased from 50 to 200 mg/L. As a heterogeneous reaction, the increase in pyrite dosage will expand the contact surface, which rapidly accelerates the H_2O_2 catalysis, and the increase in the concentration of aqueous Fe(II) might be another reason. Some complexes may form on the surface, and pyrite acts as an electron acceptor to regenerate the reactive sites (Xue *et al.* 2009).

Influence of initial pH

Heterogeneous catalysis reactions were carried out in the presence of 100 mg/L pyrite, 1 mM H_2O_2 , and pH between 3 and 9. The pH was found to be the key parameter for effective performance of pyrite-catalyzed reactions. The

degradation rate of CAP in acidic solution was more rapid than that in neutral and alkaline solutions according to Figure 1(d). At the initial stage, the degradation of CAP was mainly due to the Fenton reaction, and the reaction was more efficient in acidic conditions. The optimum pH value for both Fenton reactions is about 2.5–3.0 (Hsueh *et al.* 2005). A significant decrease in CAP degradation was clearly noted upon increasing the pH above 4. An increase in the pH value promotes the decomposition of H_2O_2 to O_2 and H_2O (Elshafei *et al.* 2014). Heterogeneous reactions would occur at the second stage, and the heterogeneous reaction occurs slowly. Thus, good treatment performance may be achieved with longer reaction times.

The reaction mechanism

As shown in Figure 2(a), the concentration of SO_4^{2-} increased rapidly in the first 10 minutes, and then increased slowly. Pyrite may be oxidized by oxygen in the environment, and the reaction may occur on the pyrite surface.

A large amount of SO_4^{2-} would exist at the initial stage for $2\text{FeS}_2(\text{s}) + 7\text{O}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{Fe}^{2+} + 4\text{SO}_4^{2-} + 4\text{H}_3\text{O}^+$ (Sit *et al.* 2012). In this reaction system, pyrite is oxidized by hydrogen dioxide to produce Fe^{2+} and SO_4^{2-} .

Large amounts of fresh Fe^{2+} would be produced according to the reaction $\text{Fe}_{1-x}\text{S} + (2-1/2)x\text{O}_2 + x\text{H}_2\text{O}_2 = (1-x)\text{Fe}^{2+} + 4\text{SO}_4^{2-} + 2x\text{H}^+$ (Nicholson & Scharer 1994). The Fe^{2+} can also react with H_2O_2 to create hydroxyl radicals by the Fenton reaction, $\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \cdot\text{OH} + \text{Fe}^{3+} + \text{OH}^-$, $\text{Fe}^{2+} + \cdot\text{OH} \rightarrow \text{Fe}^{3+} + \text{OH}^-$ (Kiwi *et al.* 2000). The pyrite may act as a 'bond' between Fe^{3+} and H_2O_2 , with Fe^{3+} accepting electrons from pyrite and the resulting Fe^{2+} donating electrons to H_2O_2 . The oxidation maintains high speed for the reaction:

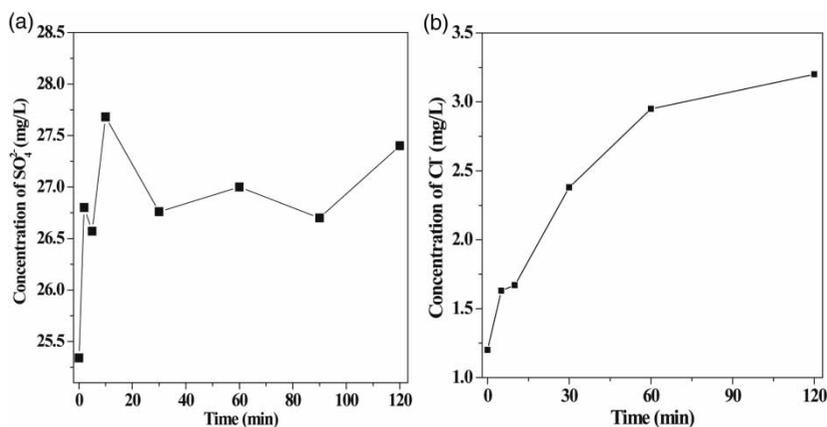


Figure 2 | Concentration of SO_4^{2-} versus reaction time in pyrite suspension. Reaction conditions: pyrite 100 mg/L, H_2O_2 1 mM, initial pH 4 (a). Concentration of Cl^- at different time. The reaction were pyrite 100 mg/L, H_2O_2 1 mM, and initial pH = 4 (b).

$\text{FeS}_2 + 14\text{Fe}^{3+} + 24\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}_3\text{O}^+$ (Cohn *et al.* 2004). Hydrogen ions are produced during the reaction, and the pH of the solution decreases.

Pyrite may be oxidized by oxygen in moist environments, and some Fe^{2+} is contained on the surface of pyrite (Sit *et al.* 2012). At the initial stage, Fe^{2+} reacts with hydrogen dioxide to oxidize pollutants, and heterogeneous Fenton reactions may occur between pyrite and H_2O_2 .

ESR spectroscopy was used to detect $\cdot\text{OH}$ in the system. The quartet structure of the DMPO-OH adduct was shown as a four-line signal, having a peak height ratio of 1:2:2:1. This matches the structure of a typical ESR spectrum of $\cdot\text{OH}$ (Sinha *et al.* 2014) as shown in Figure 3(a). This means that $\cdot\text{OH}$ exists in the system. The $\cdot\text{OH}$ leads to the oxidative degradation of CAP in the pyrite-catalyzing process. The intensity of $\cdot\text{OH}$ peaks decreased and new peaks appeared beside the four-line signal as a function of time. As stated above, in a pyrite- H_2O_2 -CAP reaction, $\cdot\text{OH}$ plays the dominant role.

To understand the degradation pathway of CAP through pyrite-catalyzed reactions, intermediates formed during the reaction were analyzed by GC/MS. This shows that the peak of CAP almost disappeared after the reaction. Intermediates such as nitrobenzaldehyde increased during the reaction. The intermediates formed in this study indicate that C-N and C-C cleavage occurred at first during the oxidative degradation of CAP (Figure 3). The CAP then transformed to nitrobenzaldehyde and dichloroacetamide by $\cdot\text{OH}$ attack. The intermediates were finally mineralized. To investigate the mineralization of CAP, the concentration of chloride ions was measured during the reaction (Figure 2(b)) and was found to significantly increase as the reaction proceeded. The concentration of chloride ions

was 2.67-fold higher than baseline after 2 hours. Significant release of chloride ions during the oxidation of CAP indicates that dichloroacetamide may be further oxidized to oxalic and formic acids or completely mineralized to HCl, CO_2 , and a small amount of simple inorganic compounds (Guo *et al.* 2002; Kanel *et al.* 2003). The total organic carbon (TOC) of 50 mg/L CAP (the initial solution) was 23.69 mg/L and the TOC of effluent after being treated for 2 h decreased to 11.36 mg/L, which shows that only part of intermediates were degraded completely.

Characterization of pyrite

As Figure 4 shows, natural pyrites are crushed particles covered with flocs that might be iron salts or some iron hydroxyl-oxide (Figure 4(a)). The main elements of pyrite are iron and sulfur. According to energy dispersive spectrometry (EDS), the ratio of iron to sulfur is 32.4:67.6. The main metallic elements of pyrite were determined by ICP. As shown in Table S2 (available online at <http://www.iwaponline.com/wst/072/202.pdf>), iron is the most common metallic element in pyrite, followed by manganese. As the main component of pyrite, iron could catalyze H_2O_2 to produce hydroxyl radicals, which could degrade organic pollutants to inorganic substances (Lin *et al.* 2014). Pyrite after the reaction has a remarkable change in texture and particle size versus the surface of natural pyrite. The ratio of iron and sulfur changed from 32.4:67.6 to 40.6:59.4, which implies that some of the components participate in the reaction. Both Fe and S on the surface of pyrite could react with Fe^{3+} or H_2O_2 in solution, but the proportion of Fe and S involved in the reaction was not the same as it was in pyrite (generally 1:2), which is the main reason for

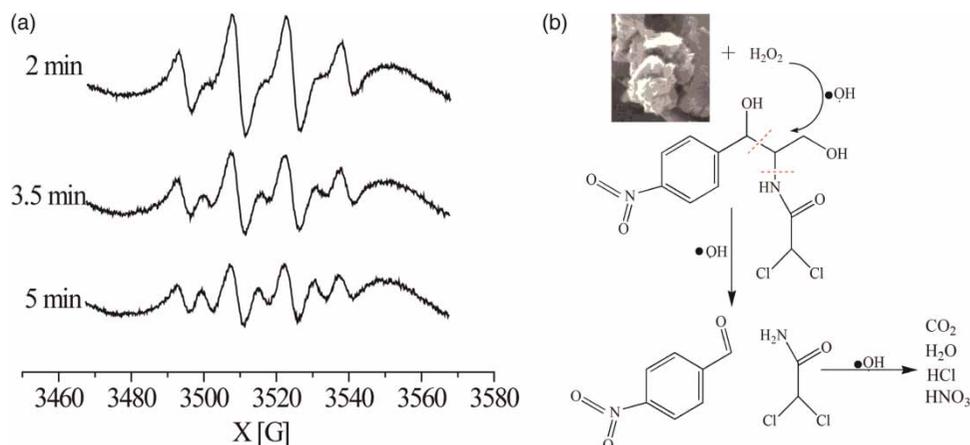


Figure 3 | ESR spectroscopy of pyrite-catalyzed H_2O_2 system (a). The degradation pathway of CAP (b).

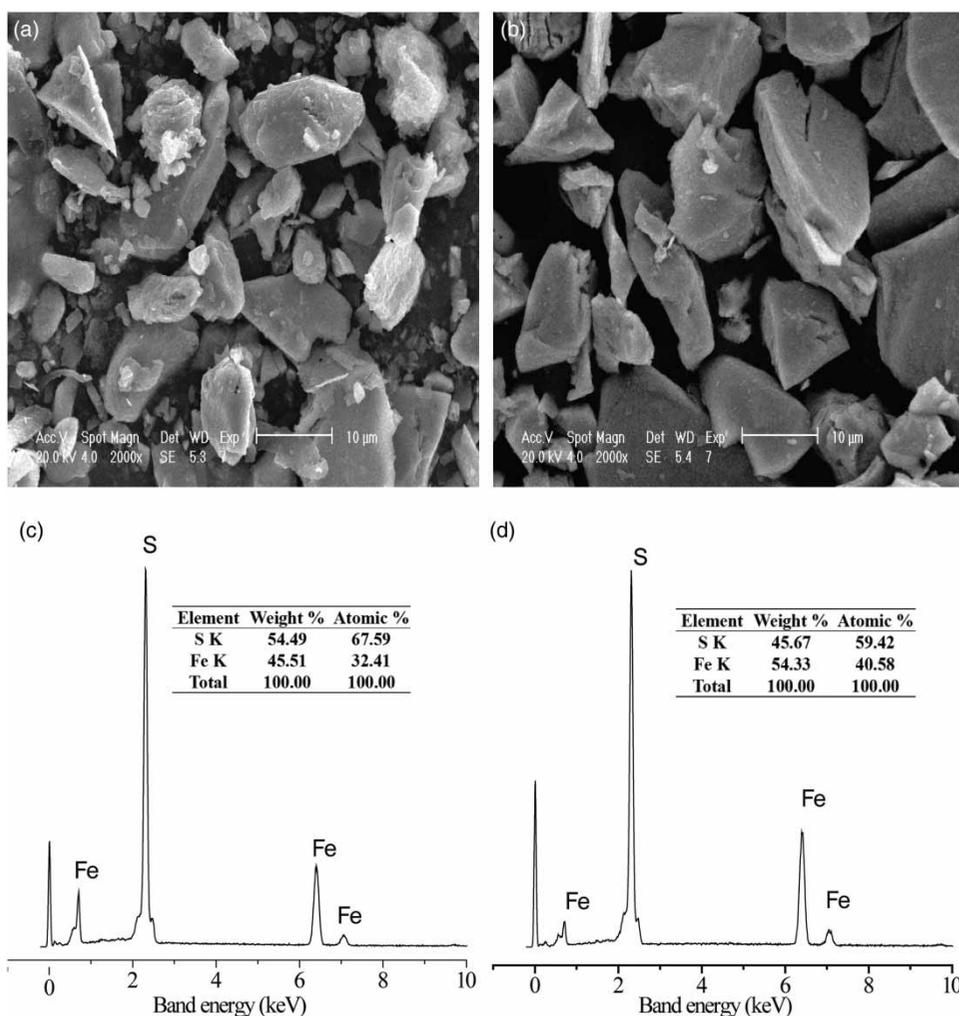


Figure 4 | Scanning electron microscopy (SEM) images of natural pyrite (a), SEM images of pyrite after reaction (b), EDS images of natural pyrite (c), and EDS images of pyrite after reaction (d).

the change of ratio. The ratio between iron and sulfur may directly influence the treatment efficiency.

CONCLUSIONS

Pyrite-catalyzed H_2O_2 processes have turned out to be a promising treatment option for CAP-contaminated water remediation. The ESR data show the presence of $\cdot OH$, which suggests that the pyrite-catalyzed H_2O_2 reaction is a hydroxyl radical reaction. The intermediates, such as nitrobenzaldehyde and dichloroacetamide, were determined during the reaction. Increasing the chloride concentration confirmed that the intermediates can be oxidized further by the pyrite-catalyzed H_2O_2 system. Pyrite acts as a 'bond' between Fe^{3+} and H_2O_2 . It is a key factor for improving the

efficiency of H_2O_2 . The pyrite-catalyzed H_2O_2 reaction continues to form hydroxyl radicals and inhibit the quenching reaction. Therefore, pyrite-catalyzed H_2O_2 can overcome the limitations of conventional advanced oxidation processes at low H_2O_2 concentrations. These results highlight the potential applications in treating refractory organic wastewater.

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REFERENCES

- Bae, S., Kim, D. & Lee, W. 2013 Degradation of diclofenac by pyrite catalyzed Fenton oxidation. *Applied Catalysis B-Environmental* **134**, 93–102.
- Benetoli, L. O. D., Cadorin, B. M., Baldissarelli, V. Z., Geremias, R., de Souza, I. G. & Debacher, N. A. 2012 Pyrite-enhanced methylene blue degradation in non-thermal plasma water treatment reactor. *Journal of Hazardous Materials* **237**, 55–62.
- Chatzitakis, A., Berberidou, C., Paspaltsis, I., Kyriakou, G., Sklaviadis, T. & Poullos, I. 2008 Photocatalytic degradation and drug activity reduction of chloramphenicol. *Water Research* **42** (1–2), 386–394.
- Che, H. & Lee, W. 2011 Selective redox degradation of chlorinated aliphatic compounds by Fenton reaction in pyrite suspension. *Chemosphere* **82** (8), 1103–1108.
- Cohn, C. A., Borda, M. J. & Schoonen, M. A. 2004 RNA decomposition by pyrite-induced radicals and possible role of lipids during the emergence of life. *Earth and Planetary Science Letters* **225** (3–4), 271–278.
- Daughton, C. H. & Ternes, T. A. 2000 Special Report: Pharmaceuticals and personal care products in the environment: agents of subtle change? (vol. 107, pg. 907, 1999). *Environmental Health Perspectives* **108**, 598.
- Elshafei, G. M. S., Yehia, F. Z., Dimitry, O. I. H., Badawi, A. M. & Eshaq, G. 2014 Ultrasonic assisted-Fenton-like degradation of nitrobenzene at neutral pH using nanosized oxides of Fe and Cu. *Ultrasonics Sonochemistry* **21** (4), 1358–1365.
- Festing, M. F. W., Diamanti, P. & Turton, J. A. 2001 Strain differences in haematological response to chloramphenicol succinate in mice: implications for toxicological research. *Food and Chemical Toxicology* **39** (4), 375–383.
- Guo, Y. H., Hu, C. W., Jiang, S. C., Guo, C. X., Yang, Y. & Wang, E. 2002 Heterogeneous photodegradation of aqueous hydroxy butanedioic acid by microporous polyoxometalates. *Applied Catalysis B-Environmental* **36** (1), 9–17.
- Hernando, M. D., Mezcuca, M., Fernandez-Alba, A. R. & Barcelo, D. 2006 Environmental risk assessment of pharmaceutical residues in wastewater effluents, surface waters and sediments. *Talanta* **69** (2), 334–342.
- Hsueh, C. L., Huang, Y. H., Wang, C. C. & Chen, C. Y. 2005 Degradation of azo dyes using low iron concentration of Fenton and Fenton-like system. *Chemosphere* **58** (10), 1409–1414.
- Huang, R. X., Fang, Z. Q., Yan, X. M. & Cheng, W. 2012 Heterogeneous sono-Fenton catalytic degradation of bisphenol A by Fe₃O₄ magnetic nanoparticles under neutral condition. *Chemical Engineering Journal* **197**, 242–249.
- Kanel, S. R., Neppolian, B., Choi, H. & Yang, J. W. 2003 Heterogeneous catalytic oxidation of phenanthrene by hydrogen peroxide in soil slurry: kinetics, mechanism, and implication. *Soil & Sediment Contamination* **12** (1), 101–117.
- Kiwi, J., Lopez, A. & Nadtochenko, V. 2000 Mechanism and kinetics of the OH-radical intervention during Fenton oxidation in the presence of a significant amount of radical scavenger (Cl⁻). *Environmental Science & Technology* **34** (11), 2162–2168.
- Liang, B., Cheng, H. Y., Kong, D. Y., Gao, S. H., Sun, F., Cui, D., Kong, F. Y., Zhou, A. J., Liu, W. Z., Ren, N. Q., Wu, W. M., Wang, A. J. & Lee, D. 2013 Accelerated reduction of chlorinated nitroaromatic antibiotic chloramphenicol by biocathode. *Environmental Science & Technology* **47** (10), 5353–5361.
- Lin, Z. R., Ma, X. H., Zhao, L. & Dong, Y. H. 2014 Kinetics and products of PCB28 degradation through a goethite-catalyzed Fenton-like reaction. *Chemosphere* **101**, 15–20.
- Nicholson, R. V. & Scharer, J. M. 1994 Laboratory studies of pyrrhotite oxidation-kinetics. In: *Environmental Geochemistry of Sulfide Oxidation (Vol. 550, Acs Symposium Series)* (C. N. Alpers & D. W. Blowes, eds). American Chemical Society, Washington, pp. 14–30.
- Ronning, H. T., Einarsen, K. & Asp, T. N. 2006 Determination of chloramphenicol residues in meat, seafood, egg, honey, milk, plasma and urine with liquid chromatography-tandem mass spectrometry, and the validation of the method based on 2002/657/EC. *Journal of Chromatography A* **1118** (2), 226–233.
- Sinha, B. K., Leinisch, F., Bhattacharjee, S. & Mason, R. P. 2014 DNA cleavage and detection of DNA radicals formed from hydralazine and copper(II) by ESR and immuno-spin trapping. *Chemical Research in Toxicology* **27** (4), 674–682.
- Sit, P. H. L., Cohen, M. H. & Selloni, A. 2012 Interaction of oxygen and water with the (100) surface of pyrite: mechanism of sulfur oxidation. *Journal of Physical Chemistry Letters* **3** (17), 2409–2414.
- Sun, F., Liu, H., Liang, B., Song, R. T., Yan, Q. & Wang, A. J. 2013 Reductive degradation of chloramphenicol using bioelectrochemical system (BES): a comparative study of abiotic cathode and biocathode. *Bioresource Technology* **143**, 699–702.
- Xue, X. F., Hanna, K., Abdelmoula, M. & Deng, N. S. 2009 Adsorption and oxidation of PCP on the surface of magnetite: kinetic experiments and spectroscopic investigations. *Applied Catalysis B-Environmental* **89** (3–4), 432–440.
- Zhang, J. W., Fu, D. F., Xu, Y. D. & Liu, C. Y. 2010 Optimization of parameters on photocatalytic degradation of chloramphenicol using TiO₂ as photocatalyst by response surface methodology. *Journal of Environmental Sciences - China* **22** (8), 1281–1289.
- Zhang, Y. L., Zhang, K., Dai, C. M., Zhou, X. F. & Si, H. P. 2014 An enhanced Fenton reaction catalyzed by natural heterogeneous pyrite for nitrobenzene degradation in an aqueous solution. *Chemical Engineering Journal* **244**, 438–445.

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