



# An enhanced Fenton reaction catalyzed by natural heterogeneous pyrite for nitrobenzene degradation in an aqueous solution

Yalei Zhang<sup>a</sup>, Ke Zhang<sup>a</sup>, Chaomeng Dai<sup>a,b,\*</sup>, Xuefei Zhou<sup>a,\*</sup>, Huiping Si<sup>a</sup>

<sup>a</sup>State Key Laboratory of Pollution Control and Resource Reuse, Tongji University, Shanghai 200092, China

<sup>b</sup>College of Civil Engineering, Tongji University, Shanghai 200092, China

## HIGHLIGHTS

- A Fenton reaction was catalyzed by the natural iron sulfur mineral pyrite.
- The degradation of nitrobenzene was significantly enhanced by the pyrite Fenton reaction.
- The initial pH has little effect on the nitrobenzene degradation in the pyrite Fenton system.
- The Fe(II) concentration was maintained at a low but sufficient amount in the pyrite Fenton system.
- Hydroxylation products were the major oxidation products detected by GC–MS.

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## ABSTRACT

Due to the limitations such as sludge formation and early termination exist in the classic Fenton reaction, an enhanced Fenton system catalyzed by heterogeneous pyrite was used to degrade nitrobenzene in this study. The results demonstrated that the degradation of nitrobenzene by the pyrite Fenton system (80%) was significantly enhanced compared to that demonstrated by a classic Fenton system. The appropriate Fe(II) concentration generated by constant dissolution from a pyrite surface and by recycling Fe(III) contributed to this enhancement. The degradation of nitrobenzene in the pyrite Fenton reaction can be properly described by pseudo-first-order kinetics, whereas that in the classic Fenton system exhibited an early termination of the nitrobenzene degradation. The degradation kinetics of nitrobenzene in the pyrite Fenton reaction was obviously influenced by the concentrations of pyrite, H<sub>2</sub>O<sub>2</sub> and nitrobenzene. However, no obvious effect of the initial pH on the degradation kinetics of nitrobenzene was observed in the pyrite Fenton reaction due to the production of hydrogen accompanied by aqueous Fe(II) generation. Degradation of the nitrobenzene was obviously inhibited by the addition of t-butanol (OH<sup>•</sup> scavenger), suggesting that nitrobenzene was dominantly oxidized by HO<sup>•</sup> generated in the pyrite Fenton system. Phenol, 2-nitrophenol, 3-nitrophenol and 4-nitrophenol were the major transformation products detected in the system, due to the attack of hydroxyl radicals to the aromatic ring and nitro group of nitrobenzene.

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## 1. Introduction

Nitrobenzene is widely used in explosives, pesticides, paper pulp production and colorant industrial processes [1–5]. Nitrobenzene is usually found in wastewater and has been listed as a priority pollutant due to the compound's mutagenesis and carcino-

\* Corresponding authors. Address: State Key Laboratory of Pollution Control and Resource Reuse, Tongji University, Shanghai 200092, China (C. Dai). Tel./fax: +86 21 65985811.

E-mail address: [chaomeng\\_dai@163.com](mailto:chaomeng_dai@163.com) (C. Dai).

genesis [6]. The persistence of nitrobenzene in the natural environment has been a serious environmental concern. However, nitrobenzene is refractory to conventional chemical oxidation because the electron-withdrawing property of the nitro group is notably strong. In addition, nitrobenzene is also resistant to conventional biological treatments due to the compound's toxic and mutagenic effects on biological systems [7,8]. Therefore, the search for an effective method of nitrobenzene removal becomes increasingly important.

In the last decade, advanced oxidation processes (AOPs) have become important technologies for water treatment [9,10] and

have been reported for the effective destruction of refractory pollutants, such as nitro-aromatic compounds [2]. The Fenton reaction has attracted wide attention among the advanced oxidation processes due to this reaction's strong oxidative capacity for the degradation of organic contaminants [11,12]. Despite its strong oxidation capacity, the classic Fenton reaction which is catalyzed by soluble  $\text{Fe}^{2+}$  has some critical limitations 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, low pH is always required [13–15]. To overcome these drawbacks of the classic Fenton process, Fenton systems that use Fe containing solid catalysts instead of soluble  $\text{Fe}^{2+}$  have recently been developed [14,16]. With advantages over classic Fenton reactions such as less iron sludge formation, a wider working pH range and possible recycling of the iron promoter, Fenton systems catalyzed by heterogeneous Fe containing solid catalysts have received increasing attention [17–19].

Pyrite, one of the most abundant natural iron sulfur mineral on the earth's surface, can be an appropriate material to act as a heterogeneous catalyst in the Fenton reaction to degrade nitrobenzene because pyrite has been successfully used as a Fenton material for the oxidative degradation of organic contaminants. For example, Che and Bae used a pyrite Fenton system for the oxidative degradation of trichloroethylene (TCE) and diclofenac [20,21], respectively, and reported that the degradation of trichloroethylene and diclofenac were significantly improved by a pyrite Fenton system than by a classic Fenton system. The removal efficiency of TCE and diclofenac in the pyrite Fenton system were 97% and 100%, respectively, whereas these efficiencies were only 77% and 65% in the classic Fenton system [20,21]. These results provide a promising insight into the application of pyrite as a heterogeneous iron source in the Fenton reaction for the removal of organic contaminants.

However, a systematic study of the degradation of nitrobenzene by a pyrite Fenton system is unavailable, and information that could be used to understand the mechanism of nitrobenzene degradation by a pyrite Fenton reaction is limited. Therefore, the major objective of this study was to investigate the reactivity of Fenton oxidation catalyzed by heterogeneous pyrite for the removal of nitrobenzene. This report is the first to describe the degradation of nitrobenzene through Fenton oxidation catalyzed by pyrite. The reactivity performance between a pyrite Fenton system and a classic Fenton system when given the same initial conditions (iron content,  $\text{H}_2\text{O}_2$  concentration, initial pH) was compared, and the effects of the pyrite,  $\text{H}_2\text{O}_2$  and nitrobenzene concentrations and of the initial pH on the degradation kinetics were evaluated in detail. Finally, the transformation products and the degradation mechanism were also identified.

## 2. Experimental

### 2.1. Chemicals and materials

Nitrobenzene (>99%), NaOH, HCl and ferrous sulfate heptahydrate were purchased from Sinopharm Chemical Reagent Shanghai Co., Ltd. (Shanghai, China).  $\text{H}_2\text{O}_2$  (non-stabilized, 30%) was purchased from Fisher (USA). Ultra-pure water was acquired from a Milli-Q water purification system (Millipore, Bedford, MA, USA). HPLC-grade methanol was purchased from Sigma–Aldrich (St. Louis, MO, USA). GC-grade dichloromethane (>99%, Sigma) and tert-butanol (t-butanol) (>99%, Sigma) were used as an extraction solvent for the GC–MS analysis and a hydroxyl radical ( $\text{HO}^\bullet$ ) scavenger, respectively. The pyrite used in this experiment was mined from Anhui, China and was milled by a hammermill and obtained as a 325 mesh powder (particle size <45  $\mu\text{m}$ ); this powder was directly applied without any pretreatment. All of the aqueous solutions were prepared in Milli Q-water.

### 2.2. Characterization of pyrite

The morphology of our pyrite was characterized by field emission environmental scanning electron microscopy (EFEG–SEM, Model Quanta 200 FEG, manufacturer FEI). The crystal structure of our pyrite was characterized by X-ray diffraction (XRD) analysis using a Bruker D8 Advance X-ray diffraction instrument ( $\text{Cu K}\alpha$ ); the scan range of the diffraction angle ( $2\theta$ ) was 25–80°. The elemental analysis was performed by X-ray photoelectron spectroscopy (XPS) equipped with a Perkin Elmer PHI 5000 ESCA System with Al  $\text{K}\alpha$  radiation at 1486.6 eV. The specific surface area of the sample was measured by BET analysis.

A scanning electron microscopy (SEM) image of the pyrite revealed the non-uniform shape of micro-size particles (0.5–3  $\mu\text{m}$ ) (Fig. 1(a)). X-ray diffraction (XRD) analysis of the pyrite showed a good agreement with that in the Joint Committee on Powder Diffraction Standards (JCPDS) diffraction data files (JADE 9, Materials Data Inc.) (Fig. 1(b)). Elemental analyses showed that the iron content of the pyrite was 24.67%, and BET analysis showed that the surface area of pyrite was 3.989  $\text{m}^2/\text{g}$ .

### 2.3. Degradation of nitrobenzene by the pyrite Fenton system and the classic Fenton system

Experiments to investigate the degradation of nitrobenzene in the pyrite Fenton reaction were conducted in capped brown glass

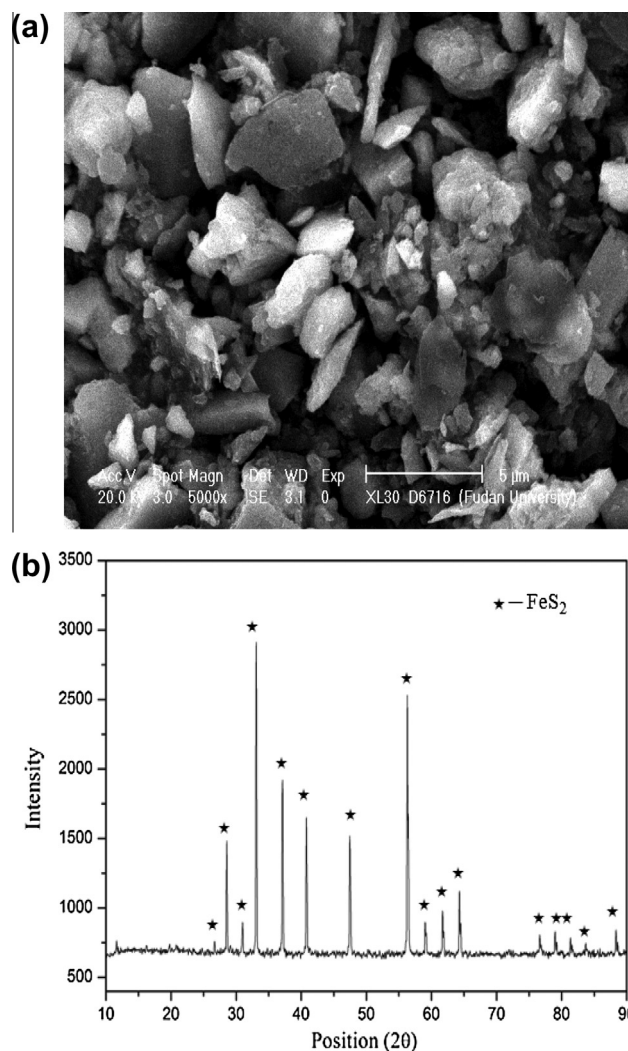


Fig. 1. SEM (a) and XRD (b) images of pyrite.

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