



Enhanced oxidation of chloramphenicol by GLDA-driven pyrite induced heterogeneous Fenton-like reactions at alkaline condition



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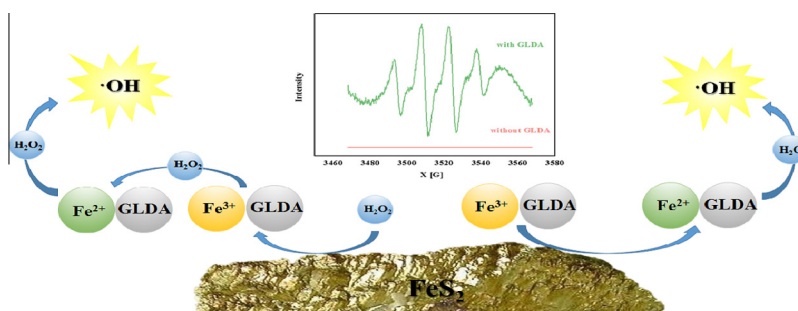
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HIGHLIGHTS

- Novel combination of abundant mineral FeS₂ and environmentally-benign complexing agent GLDA.
- Significantly enhanced efficiency of Fenton-like reaction at alkaline condition.
- Promoted formation of ·OH as the predominant reactive radicals with GLDA.
- Fe³⁺-GLDA interacted with FeS₂ accelerating the Fe(III)/Fe(II) cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

The influence of a biodegradable agent, N,N-bis(carboxymethyl)glutamic acid (GLDA), on chloramphenicol (CAP) degradation in pyrite/H₂O₂ system was investigated. The results indicated that the presence of GLDA could extend the working pH range and provided favorable performance at alkaline conditions. The addition of 100 μmol/L GLDA increased the CAP removal rate to 83.3% at pH 8 due to the reinforced formation of ·OH. The beneficial effect was found to be indifferent of possible reduction of redox potential (Fe(III)/Fe(II)), probable decrease of reaction pH and complex of structured iron on pyrite surface. However, it was correlated well with the facilitated autocatalytic oxidation reaction by Fe(III)-GLDA that promoted cycle of iron, which was confirmed by the determination of ESR and sulfate ion leaching. Based on GC-MS results, the presence of GLDA led to further oxidation of product with reinforced oxidation efficiency, and the potential degradation routine remains similar. All these provide some fundamental insights into the characteristics of environment friendly GLDA-enhanced pyrite/H₂O₂ system for bio-refractory contaminants removal under neutral or alkaline conditions, and enrich the theoretical knowledge of heterogeneous Fenton-like processes.

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1. Introduction

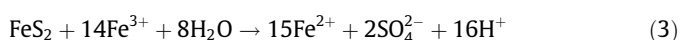
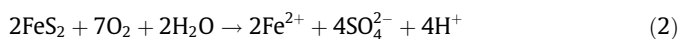
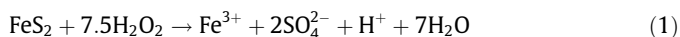
Advanced oxidation processes (AOPs), such as Fenton and Fenton-like processes, have been extensively investigated in biorefractory contaminants removal [1]. To overcome the demerits of ferric hydroxide sludge formation and prerequisite acidic condition

in homogeneous Fenton reactions [2,3], iron oxides including ferrihydrite, goethite, hematite, pyrite and magnetite were used over a wider pH range [4–7]. However, heterogeneous Fenton-like catalysts tend to show undesirable catalytic activity, especially at alkaline conditions. It is reported that Fe₃O₄ magnetic nanoparticles could remove over 85% phenol at low pH (<3) but its catalytic efficiency decreased sharply (below 10%) at high pH (>4) [8]. Additionally, inefficient TNT abatement (below 20%) occurred at pH 7 in mineral-catalyzed systems including ferrihydrite,

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lepidocrocite and hematite [7]. Thus, the development of efficient Fenton oxidation strategies at alkaline pH has attracted considerable attention.

Pyrite (FeS_2) is among the most effective catalysts due to Fe(II)-rich structure and was used to decompose H_2O_2 to degrade 2,4,6-trinitrotoluene [7], trichloroethylene [9], carbon tetrachloride [10], azo dyes [11] and pyrene [12]. Besides generally-accepted chain reactions in iron-bearing mineral catalyzed systems, the better catalytic activity of pyrite is attributed to the autocatalytic dissolution and oxidation, described in the following reactions [13]:



Although Fe^{2+} is generated when pyrite reacts with O_2 (Eq. (2)) and Fe^{3+} (Eq. (3)), pyrite oxidation rate is much faster at Eq. (3), which can only occur at acidic pH [14]. Indeed, neutral or alkaline conditions impedes pyrite catalytic reaction, though pyrite is less sensitive to pH compared to homogeneous Fenton processes [15]. Hence, it can be presumed that Eq. (3) is the rate-limiting step at alkaline condition, and pyrite catalytic activity could be improved by reinforcing this reaction.

In addition to low catalytic efficiency when $\text{pH} \geq 7$, another disadvantage is that excessive amount of H_2O_2 is prerequisite for desirable degradation efficiency. The combination of chelating agents (CAs) with Fenton reactions has been regarded as potential strategy. The presence of ethylenediaminetetraacetic acid (EDTA) in homogeneous Fenton processes can boost removal of Norway spruce thermomechanical pulp [16], naphthol dyes [17], and pentachlorophenol (PCP) [18]. The degradation rate for organic contaminants was reinforced by complexes of Fe(II) and glutamate [19], glutamic acid [20] and cross-linked chitosan [21]. The addition of ethylenediamine-*N,N'*-disuccinic acid (EDDS) extended the working range of Fe(III)/ H_2O_2 to neutral pH and improved the depletion of bisphenol A (BPA) [22]. Previous literature reported that ligand-enhanced oxidation rate of organic pollutants also occurred in heterogeneous systems. Existing nitrilotriacetic acid (NTA) can increase the removal efficiency of carbamazepine in nano- $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ system [23], while EDDS inhibited heterogeneous Fenton degradation of BPA using goethite as iron source [24]. BPA degradation efficiency in the combination of nano-sized BiFeO_3 with chelating agents had the order: EDTA > NTA > glycine > formic acid > tartaric acid > none chelating agent [25]. PCP degradation using micro-sized magnetite and CAs has rates in the following order: oxalate > EDTA > carboxy-methyl- β -cyclodextrin > citric acid > tartaric acid > succinic acid > none chelating agent [26]. The positive impact of the CAs in Fenton systems is obvious. One explanation is that the CAs could limit iron precipitation and improve iron dissolution from solid surface. Moreover, the propagation of homogeneous reaction by dissolved iron-ligands accelerated the production of reactive oxidizing species [23,26,27]. Another explanation is that $\cdot\text{OH}$ facilitated formation on solid surface is responsible for higher degradation efficiency [23,25]. In conclusion, understanding of the mechanism is still inconsistent.

Most of the reported organic ligands, such as EDTA [17], pyrophosphate, citrate [28], and EDDS [22], may be of low biodegradability, high cost or vulnerable to photochemical reactions. *N,N*-bis(carboxymethyl)glutamic acid (GLDA) is classified as environmentally-friendly, aminopolycarboxylate CA according to the internationally recognized OECD 301D test [29] and was used to complex with heavy metal removal [30–32]. GLDA was chosen as the representative CA in this research because it is more

biodegradable (>60% degraded within 28 days) than EDTA and much cheaper than EDDS. Chloramphenicol (CAP) has been selected as a target contaminant, since CAP is a broad-spectrum antibiotic drug widely existing in aqueous and soil environment [33].

The primary concerns of this study were to verify the following questions: (i) can heterogeneous Fenton-like reaction with pyrite be reinforced by GLDA over various pH conditions; (ii) can the boosted activation be efficient for the degradation of pollutants at alkaline pH; and (iii) what is the underlying mechanism of the activation process. Based on the above consideration, this research was originally conducted to investigate: (i) the impact of GLDA on pyrite, H_2O_2 , pyrite/ H_2O_2 system; (ii) the influence of GLDA, pyrite, H_2O_2 concentration and the initial pH on the degradation of CAP; (iii) the comparative catalytic ability of GLDA-pyrite/ H_2O_2 heterogeneous and GLDA- Fe^{2+} homogeneous Fenton systems; (iv) the change of redox potential of $\text{Fe}^{3+}/\text{Fe}^{2+}$ in the presence of GLDA; (v) the determination of predominant radicals in this system; (vi) the differences of pH variation and concentration variation of sulfate radical anion between GLDA-pyrite/ H_2O_2 and pyrite/ H_2O_2 systems; (vii) the structure transformation of pyrite confirmed by ATR-FITR. The objective of this study is to develop a highly efficient heterogeneous Fenton-like system working over a wide pH range and provide insight into the mechanism.

2. Experimental section

2.1. Chemicals and materials

Hydrogen peroxide (30%, w/w), sulfuric acid, sodium hydroxide and ferrous sulfate heptahydrate of analytical grade were supplied by Chemicals Corporation (Shanghai, China). Methanol of HPLC grade was purchased from ANPEL Scientific Instrument Co., Ltd (Shanghai, China) (Table 1). CAP of HPLC grade was obtained from J&K Chemical Co., Ltd (Beijing, China). *N,N*-bis(carboxymethyl)glutamic acid tetrasodium salt (GLDA) of analytical grade was purchased from Tokyo Chemical Industry (Table 1). All solutions were prepared with 18 M Ω Milli-Q water from a Millipore system (Bedford, USA). The natural pyrite sample was obtained from LvLing Chemical Industry Group Co., Ltd. (Jiangsu, China).

2.2. Oxidation procedure

Experiments were performed in 250 mL reaction flasks with constant magnetic stirring at room temperature (25 ± 2 °C). In all the cases, 200 mL CAP (50 mg/L) solution contained appropriate amounts of pyrite powder and GLDA, and then the solution pH was adjusted by NaOH and H_2SO_4 . The reaction started when H_2O_2 was added to the solution with magnetic stirring to keep the pyrite suspended. At specific time intervals, 1 mL samples were withdrawn and 10 μL methanol was added to terminate reaction. The samples were filtered with 0.45 μm filters (ANPEL Scientific Instrument Co., Ltd, Shanghai) to remove pyrite particles. Control experiments were conducted without the addition of pyrite, H_2O_2 or GLDA. In contrast, homogeneous Fenton process were conducted by adding 5 mg or 34.8 mg ferrous sulfate heptahydrate, which is equivalent to dissolved iron ions and iron-element content of initial pyrite, to CAP solution.

2.3. Analytical procedures

The CAP was measured with an Agilent 1260 liquid chromatography system equipped with a quaternary solvent delivery system, an auto sampler, and a DAD detector (HPLC). Elution was performed on an Agilent Eclipse XDB C18 column (5 μm ;

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