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Ascorbic acid enhanced activation of oxygen by ferrous iron: A case of aerobic degradation of rhodamine B

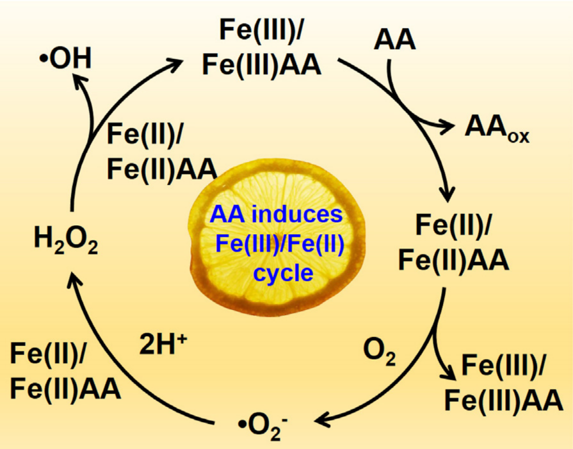
Xiaojing Hou, Wenjuan Shen, Xiaopeng Huang, Zhihui Ai*, Lizhi Zhang

Key Laboratory of Pesticide & Chemical Biology of Ministry of Education, Institute of Environmental Chemistry, Central China Normal University, Wuhan 430079, PR China

HIGHLIGHTS

- Ascorbic acid could relieve the accumulation of Fe(III) by accelerating Fe(III)/Fe(II) cycle.
- Ascorbic acid could lower the redox potential of Fe(III)/Fe(II) through chelating effect.
- Ascorbic acid enhanced ROS generation for promoting RhB degradation.

GRAPHICAL ABSTRACT



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ABSTRACT

Molecular oxygen activation by ferrous ions (Fe(II)) in aqueous solution could generate reactive oxygen species (ROS) with high oxidation potential via reaction between Fe(II) and oxygen molecules (Fe(II)/air), however, ROS yielded in the Fe(II)/air process is insufficient for removal of organic pollutants due to the irreversible ferric ions (Fe(III)) accumulation. In this study, we demonstrate that ascorbic acid (AA) could enhance ROS generation via oxygen activation by ferrous irons (AA/Fe(II)/air) and thus improve the degradation of rhodamine (RhB) significantly. It was found that the first-order aerobic degradation rate of RhB in the AA/Fe(II)/air process in the presence of ascorbic acid is more than 4 times that of the Fe(II)/Air system without adding ascorbic acid. The presence of ascorbic acid could relieve the accumulation of Fe(III) by reductive accelerating the Fe(III)/Fe(II) cycles, as well as lower the redox potential of Fe(III)/Fe(II) through chelating effect, leading to enhanced ROS generation for promoting RhB degradation. This study not only sheds light on the effect of ascorbic acid on aerobic Fe(II) oxidation, but also provides a green method for effective remediation of organic pollutants.

1. Introduction

Iron is the forth abundant element in earth's crust. In view of its natural abundance and environmental benignancy, iron redox

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* Corresponding author. Fax: +86 27 6786 7535.
E-mail address: jennifer.ai@mail.ccnu.edu.cn (Z. Ai).

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cycling represents an important sink for environmental contaminants. For example, ferric salts are widely used for flocculation of wastewater pre-treatment due to their readily available and inexpensive nature [1–3]. Fenton reaction using ferrous ions (Fe(II)) and hydrogen peroxide (H_2O_2) as reagents has been used widely for oxidative degradation of organic pollutants [4–9]. But the Fenton procedure requires the use of acidic pH (<3) or high concentration of H_2O_2 relative to pollutants, this results in high investment and operating costs. Recently, more and more attentions have been paid to aerobic ferrous iron process (Fe(II)/air) where organic pollutants were decomposed by reactive oxygen species (ROS) from molecular oxygen (O_2) activation over ferrous ions [10–12]. Obviously, aerobic Fe(II)/air process using atmospheric oxygen molecules in place of H_2O_2 is superior and greener for environmental remediation.

In addition to biochemical catalytic oxygen activation systems [13,14], abiological oxygen activation process that relates to the cleavage of diatomic O—O bond occurs naturally in environment where iron rich waters are exposed to oxygen, as well happens in industrial oxidation. Oxygen activation by aqueous Fe(II) is thermodynamically favored and rapid under many conditions, it involves one electrons transfer from Fe(II) to oxygen to generate superoxide anion radicals ($O_2^{\bullet -}$) (Eq. (1)), followed the subsequent generation of H_2O_2 and hydroxyl radicals ($^{\bullet}OH$) (Eqs. (2)–(3)). These generated ROS could oxidatively decompose organic pollutants. Simultaneously, the oxygen activation over Fe(II) process generates Fe(III) (Eqs. (1)–(3)). Although the formed Fe(III) could be slowly recycled to Fe(II) by reaction with $O_2^{\bullet -}$ (Eq. (4)), the irreversible precipitation of Fe(III) under neutral pH conditions significantly affects the oxygen activation and slows down or blocks the ROS generation (Eqs. (1)–(3)) [15,16].

$$\mathrm{Fe(II)} + O_2 \rightarrow \mathrm{Fe(III)} + O_2^{\bullet -} \tag{1}$$

$$2O_2^{\bullet -} + 2\,H^+ + H_2O \rightarrow H_2O_2 + O_2 \tag{2}$$

$$\mathrm{Fe(II)} + H_2O_2 \rightarrow \mathrm{Fe(III)} + {}^{\bullet}OH + OH^- \tag{3}$$

$$\mathrm{Fe(III)} + O_2^{\bullet -} \rightarrow \mathrm{Fe(II)} + O_2 \tag{4}$$

For the purpose of reducing Fe(III) to Fe(II) with electron donor nature and much higher solubility, organic ligands such as ethylenediaminetetraacetic acid (EDTA) has been used to extend the useful range of the Fe(II)/air system to neutral pH conditions for preventing iron precipitation and so producing more oxidizing ROS species [17,18]. However, the application of EDTA could cause adverse environmental consequences because of its poor biodegradability and strong heavy metal chelating ability. Previously, tetrapolyphosphate (TPP), a widely used and eco-friendly food additives, was used to improve the oxidation efficiency of Fe(II)/air system as TPP could decrease the redox potential of Fe(III)/Fe(II) to generate more ROS via dioxygen reduction [19]. Recently, hydroxylamine (NH_2OH) and/or quinone were adopted to accelerate the Fe(III)/Fe(II) redox cycles during Fenton process [20,21], where NH_2OH serves as common reductive chemical to reduce Fe(III) to Fe(II), while quinone could reduce and chelate with Fe(III) simultaneously. But NH_2OH is a toxic compound containing nitrogen element, which could lead to environmental eutrophication problem. Meanwhile, quinone is of high cost and far from practical application. Therefore, it is urgent to develop greener method to promote Fe(II)/Fe(III) cycles and oxygen activation performance of Fe(II)/air for its practical application.

Ascorbic acid (2-oxo-L-threohexono-1,4-lactone-2,3-enediol, AA) is a water soluble vitamin that has gained importance over years as a primary or natural antioxidant. Many electron donors like H_2O_2, Fe(III), and Cu(II) could be reduced by AA [22–24]. In addition, AA has the ability to solubilize metal ions by complex formation [25]. Previously, AA was found to promote the reductive dissolution of goethite, which then facilitated the chemical reduction of 4-cyanonitrobenzene [26]. According to AA's double faced character, it is expected that the presence of AA could prevent iron precipitation and thus produce more ROS to realize the real application of Fe(II)/air process in environmental remediation.

In this study, we developed an efficient AA/Fe(II)/air organic pollutants degradation system. The presence of ascorbic acid could relieve the accumulation of Fe(III) by reductive accelerating the Fe(III)/Fe(II) cycles, as well as lower the redox potential of Fe(III)/Fe(II) through chelating effect, leading to enhanced ROS generation in the AA/Fe(II)/air system. Nowadays, dyes release is still a matter continuing concern, most dyes are resistant to biodegradation and self-degradation in the ecosystem [27]. Thus, we choose rhodamine B as the targeted pollutant to investigate its degradation dynamics in the AA/Fe(II)/air system. The mechanism involved in the oxygen activation process are proposed.

2. Chemicals and methods

2.1. Chemicals

L-Ascorbic acid (AA), $FeSO_4{\cdot}7H_2O$, Rodamine B (RhB), 1,10-phenanthroline, and ethylene diamine tetraacetic acid (EDTA) were all analytic reagent and purchased from Sinopharm Chemical Reagent Co., Ltd., China. *N*,*N*-dethyl-1,4-phenylene-diamine (DPD) was obtained from Alfa-Aesar, USA. Superoxide dismutase (SOD) came from Sigma–Aldrich (St. Louis, MO). Horseradish peroxidase (POD, specific activity of 100 units m^{-1}), terephthalic acid (TA) and 2-hydroxyterephthalic acid (TAOH) were analytic reagent ordered from Aladdin Chemistry Co., Ltd., China. Methanol (HPLC grade) was purchased from Tedia Company, Inc., USA. Deionized water was used throughout the experiments.

2.2. Aerobic oxidation procedure

The aerobic RhB degradation was carried out in 50 mL conical flasks at room temperature (25 °C). The initial pH of the RhB solution was 6 without any adjusting. In a typical AA/Fe(II)/air procedure, 100 μL of 30 mmol/L $FeSO_4{\cdot}7H_2O$ solution and 2 mg AA were introduced into 30 mL of 5 mg L^{-1} (0.01 mmol L^{-1}) RhB solution in the conical flasks with a flow of 1.5 L/min air bubbling via a plastic pipe. Samples were collected at regular intervals using a 2 mL syringe and filtered through a 0.22 μm nylon syringe filter for analysis immediately. For comparison, experiments with $FeSO_4{\cdot}7H_2O$ and/or AA were conducted under identical conditions respectively. The anaerobic degradation of RhB was conducted using oxygen-free deionized water under Ar gas bubbling with a flow of 1.5 L/min. Oxygen-free or oxygen-saturated solutions were obtained by bubbling with argon or pure oxygen for 30 min before adding AA into the solution throughout the experiments. All the degradation experiments were replicated for three times.

2.3. Analytical methods

The concentration of RhB was monitored by colorimetry with a U-3310 UV–vis spectrometer (UV-2550) at an interval of 10 min. The total organic carbon (TOC) concentration during the degradation of RhB was analyzed by a Shimadzu TOC-V CPH analyzer after filtration through 0.22 μm filter. Hydrogen peroxide was analyzed using the DPD method developed by Bader et al. [28]. Typically, 0.4 mL of phosphate buffer solution (pH 6) and 0.1 mL of 0.01 mol/L bipyridine solution were premixed in a quartz cell, followed by addition of 2 mL of the sample, 30 μL of 1% DPD reagent in 0.1 mol/L H_2SO_4, and 30 μL of POD reagent successively. Then the absorbance at 551 nm was measured after the addition of the POD. Terephthalic acid (TA) was used as the fluorescent probe for the detection of hydroxyl radicals. 2-Hydroxyterephthalic acid (TAOH), which is