Ascorbic Acid Enhanced Activation of Oxygen by Ferrous Iron: A Case of Aerobic Degradation of Rhodamine B

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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.

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1. Introduction

Iron is the forth abundant element in earth's crust. In view of its natural abundance and environmental benignancy, iron redox 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 ($\text{O}_2^{\bullet-}$) (Eq. 1), followed the subsequent generation of H_2O_2 and hydroxyl radicals ($\bullet\text{OH}$) (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 $\text{O}_2^{\bullet-}$ (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].

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 (NH₂OH) and/or quinone were adopted to accelerate the Fe(III)/Fe(II) redox cycles during Fenton process [20-21], where NH₂OH serves as common reductive chemical to reduce Fe(III) to Fe(II), while quinone could reduce and chelate with Fe(III) simultaneously. But NH₂OH 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 H₂O₂, 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), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, Rhodamine 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 $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution and 2 mg AA were introduced into 30 mL of 5 $\text{mg} \cdot \text{L}^{-1}$ (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 $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 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 the fluorescent product of the reaction of TA with $\bullet\text{OH}$, has a strong fluorescent emission around 426 nm when excited at 312 nm. Fluorescence spectra of the supernatant liquid were measured with a fluorescence spectrophotometer (Cary Eclipse Fluorescent Spectrometer, FL1008M018). In a typical

process, an aqueous solution with 0.01 mol/L of NaOH and 0.5 mmol/L of TA was prepared and then reacted with 2 mL of sample solution for 10 min. Subsequently, the amount of produced TAOH was determined by the fluorescence intensity. The ferrous ion concentrations in the solution were measured by a modified 1,10-phenanthroline method at a wavelength of 510 nm using a UV-vis spectrophotometer (U-3310, HITACHI) [29]. In a typical process, aqueous samples were added to 1 mL of 1, 10-phenanthroline (2 g/L) in a 1 cm quartz cell, deionized water was added to make the final volume of 3 mL. The absorbance was measured at $\lambda = 510$ nm, which is the maximal adsorption of Fe(II)-1,10-phenanthroline complex. Cyclic voltammetry (CV) was performed on a computer-controlled CHI-660C electrochemical workstation using a three-electrode cell, using a platinum electrode as the working electrode, an Ag/AgCl electrode (saturated with KCl) as the reference electrode, and a saturated calomel reference electrode (SCE) as the auxiliary electrode between -1.80 and +1.80 V. CV were recorded at a scan rate (v) of 50 mV/s in a 0.05 M KCl solution (pH = 6) containing 1 mM of Fe(II) or Fe(II)-AA. These electrolyte solutions were purged with argon for 30 min for removal of dissolved oxygen before starting the measurements. The concentrations of NO_3^- ions were detected using an ion chromatograph (IC, Dionex ICS-900, Thermo) equipped with an AS23 column. The intermediate products of RhB were identified by gas chromatograph-mass spectrometry (GC-MS, TRACE ISQ, Thermo) equipped with a TG-5 column (30 m $\times$ 0.25 mm ID, 0.25 μm film thickness). Electron impact (EI) was used as ionization technique with electron energy of 70 eV. Helium served as the carrier gas at a constant flow of 1.0 mL/min (He, 99.99%). The mobile phase contains 0.8 mmol L⁻¹ NaHCO₃ and 4.5 mmol L⁻¹ Na₂CO₃, with a flow rate of 1.0 mL min⁻¹. And the injection volume of samples was 10 μL . The intermediates of RhB degradation were detected by gas chromatograph- mass spectrometry (GC-MS, Trace ISQ Thermo) with a DB-5 column (30 m $\times$ 0.25 mm).

3. Results and Discussion

3.1. Aerobic Degradation of RhB.

The aerobic degradation of RhB at room temperature was performed over Fe(II)/Air, AA/Air, and AA/Fe(II)/Air processes at neutral pH. As shown in Figure 1, RhB could not degrade in the AA/Air system. 9% of RhB was removed over Fe(II)/Air, while a higher degradation of 39.5% was observed in AA/Fe(II)/Air process in 6 h. Moreover, the aerobic degradation of RhB was found to follow a pseudo-first order kinetic process. The degradation rate constants (k) in the Fe(II)/Air, AA/Air, and AA/Fe(II)/Air systems were 0.009, 0.001, and 0.107 h⁻¹, respectively; where the degradation rate of RhB in the AA/Fe(II)/Air system was more than 10 times that in the Fe(II)/Air process. These results suggested that the presence of AA could enhance the aerobic degradation of RhB significantly.

The influence of AA dosages between 0 to 4 mg on the aerobic degradation of RhB at neutral pH in the AA/Fe(II)/Air system was studied (Figure 2). It was found that the RhB degradation was 5%, 28%, 47%, 36% and 33% in the presence of AA with dosage of 0 mg, 1 mg, 2 mg, 3 mg, and 4 mg respectively. RhB degradation increased with increasing the AA dosage from 0 to 2 mg, and then decreased when the dosage of AA was higher than 2 mg in the AA/Fe(II)/Air system. Accordingly, the degradation rate constants (k) with the AA dosage of 0 mg, 1 mg, 2 mg, 3 mg and 4 mg in the AA/Fe(II)/Air systems were 0.009 h⁻¹, 0.056 h⁻¹, 0.107 h⁻¹, 0.092 h⁻¹ and 0.071 h⁻¹, respectively. AA with reductive activity could not only react with Fe(III) to promote Fe(III)/Fe(II) cycle, but also be oxidized by reactive oxygen species [30]. Thus, excess AA could capture more reactive oxygen species and inhibit the degradation of RhB. In short, an AA dosage of 2 mg was optimized for the study of aerobic RhB degradation mechanism.

3.2. AA Enhanced Aerobic ROS Generation.

In order to understand the role of oxygen on the pollutant degradation, we compared the aerobic (air bubbling) and anaerobic (argon bubbling) degradation of RhB (AA/Fe(II)/Ar). As shown in

Figure 3a, the comparison showed that RhB could not be degraded in the absence of oxygen (Figure 3a), suggesting that Fe(II) could not reductively degrade RhB directly. Moreover, TOC measurement results indicated that RhB could not be mineralized in the Fe(II)/Air process in the absence of AA. However, about 5% and 16% of TOC removal rates were observed in the AA/Fe(II)/Air system without and with the addition of RhB respectively, revealing that partial RhB was mineralized to CO₂ in AA/Fe(II)/Air system after 8 h of degradation (Figure 3b). In addition, the absorption of UV region was decreased significantly after the reaction (inset in the Figure 3b), implying the mineralization of rhodamine B in AA/Fe(II)/Air system. The above results clearly demonstrated that enhanced RhB degradation was realized in the AA/Fe(II)/Air system involving a molecular oxygen activation process in the presence of air.

We compared the H₂O₂ formed in the Fe(II)/Air and the AA/Fe(II)/Air systems (Figure 4a), it was found that the concentration of H₂O₂ increased first and then decreased in both systems. This is reasonable because H₂O₂ would be rapidly decomposed by Fe(II) via Fenton reaction (Eq. 3). Terephthalic acid (TA) was used as the fluorescent probe for the detection of •OH generated in Fe(II)/Air system and the Fe(II)/AA/Air systems (Figure 4b). The fluorescent intensity measured in the AA/Fe(II)/Air system was much higher than that in Fe(II)/Air system, revealing that AA/Fe(II)/Air could generate more •OH radicals than Fe(II)/air system via molecular oxygen activation.

Moreover, the active species trapping experiments were performed by adding *iso*-propanol (•OH scavenger), catalase (H₂O₂ scavenger), and superoxide dismutase (SOD, •O₂⁻ scavenger) as scavengers to the aerobic RhB degradation solution during the AA/Fe(II)/Air system (Figure 5). It was found that the addition of *iso*-propanol, catalase, and SOD could depress the degradation of RhB by 82.5%, 76.7%, and 61.8% respectively. Therefore, the aerobic degradation involved the generation of ROSs of •O₂⁻, H₂O₂, and •OH species, among them •OH played a key role in the

aerobic degradation of RhB in the AA/Fe(II)/Air system.

3.3. The Role of AA on Enhancing Aerobic RhB Degradation.

To investigate the role of AA on enhancing ROS generation in the aerobic AA/Fe(II)/Air process, firstly, we measured the temporal pH during the aerobic processes (Figure 6a). It was found that the pH of RhB solution decreased from an initial value of 6.8 to 6.0 after adding Fe(II) and to 4.1 after adding AA. Subsequently, the reaction pH increased slightly to a final value of about 4.3 in the AA/Fe(II)/Air system after 6 h reaction, indicating that the aerobic process was a proton consuming process (Eq. 2) during the aerobic degradation. Ascorbic acid is a weak acid and a potent antioxidant or reducing agent with the ability to solubilize metal ions by complex formation. In order to differentiate the contribution of acidify effect, reductive effect, and complex effect of AA on enhancing the aerobic degradation of RhB, the experiment using H_2SO_4 to adjust the initial pH of RhB solution to 4 was performed at first. As shown in Figure 6b, the degradation rate of RhB in the Fe(II)/Air system was nearly the same in the H_2SO_4 /Fe(II)/Air system. This result rules out the possibility that the acidify effect did not contribute to the enhancement with the addition of AA.

Moreover, as AA is a typical reducing agent, it might react with Fe(III) under some circumstances. It was reported that the oxygen activation by metal complexes was usually accompanied with an increase of the metal oxidation state, leading to depressing the activation performance. Ascorbic acid is a potent antioxidant or reducing agent that is capable of reducing Fe(III) and realizing Fe(III)/Fe(II) redox cycles in the aerobic processes. We therefore monitored the concentrations of iron species during the aerobic RhB degradation process (Figure 7). It was found that both Fe(II) concentration and total Fe concentration decreased sharply along with a slight increase of Fe(III) concentration in the Fe(II)/Air system, nearly 30% of Fe (II) was transformed into Fe (III) in the Fe(II)/Air system within 2 h, and then the concentration of Fe (III) kept relatively steady. This result confirmed that oxygen activation over Fe(II) without AA was related to consuming of Fe(II) and accumulation of

Fe(III). However, both Fe(II) concentration and total Fe concentration kept constant without Fe(III) accumulation during the whole degradation process, suggesting that reduction effect of AA would prevent the generation of iron sludge during the aerobic process. Previous studies have shown that Fe(III) could be reduced by AA in aqueous solutions below pH 4.1 [31]. Direct evidence has suggested that as the pH increases to 5 and above, the reduction rate of Fe(III) by AA becomes quite slow. Based on the aforementioned data and analysis, we could infer a possibility that the addition of AA to the aerobic system might effectively alleviate the accumulation of Fe (III), consequently increased the oxidation reactivity.

It is known that the chelation of ferrous ions with suitable ligand could significantly reduce the standard electrode potential of Fe(III)/Fe(II) to produce reactive oxygen species [32]. Thermodynamically, the standard potential (+0.77 V) of Fe(III)/Fe(II) is more positive than those (-0.33 V and +0.70 V) of $O_2/\cdot O_2^-$ and O_2/H_2O_2 , implying that ferrous ions could not activate oxygen spontaneously. It was reported that ligands that form bidentate-mononuclear complexes such as oxalate, citrate, and others with adjacent hydroxyl groups often enhance dissolution of metal surface oxides [33]. Hence, the degradation of RhB in the aerobic process in the presence of various ligand including of EDTA, DTPA, and PTA was evaluated and compared (Figure 8a). Interestingly, we found that the AA/Fe(II)/Air showed superior aerobic degradation efficiency over the other process using DTPA, EDTA, or PTA as ligands. We therefore conclude that AA is a much superior ligand for oxygen activation with readily available ferrous ions. In addition, cyclic voltammetry was performed to determine the redox potential of AA/Fe(II)/Air in this study (Figure 8b). In the Fe(II)/Air system, the two well-defined peaks were ascribed to the overall redox potentials of the Fe(III)/Fe(II) couple. The reduction peak was observed at 0 V with peak current of -1.8×10^{-5} A and the oxidation peak was at 1.0 V with peak current of 4.2×10^{-5} A. In the AA/Fe(II)/Air system, a new oxidation peak appeared at 0.51 V with peak current of 8.8×10^{-5} A. Additionally, oxidation peak of Fe(II) was no

overall changed, while the corresponding peak current increased to 9.0×10^{-5} A. The reducing potential was shifted to positive direction (from 0 to 0.23 V), indicating that oxidizing reaction will more thermodynamically favorable occur in the AA/Fe(II)/Air system.

Based on the aforementioned data and analysis, we could infer that the addition of AA to the aerobic RhB degradation system might effectively alleviate the accumulation of Fe (III), consequently increased the redox reactivity. First, AA could complex with Fe(II) to form coordination compound Fe(II)AA_x (Eq. 5), which is more thermodynamically favorable to be oxidized by molecular oxygen to produce superoxide anion radical ($\bullet\text{O}_2^-$) (Eqs. 1, 6). After that, Fe(II) or Fe(II)AA_x could react with $\bullet\text{O}_2^-$ to produce H₂O₂ and Fe(III) or Fe(III)AA_y (Eqs. 2, 7-8). Subsequently, Fe(II) or Fe(II)AA_x could decompose H₂O₂ for the generation of $\bullet\text{OH}$ (Eqs. 3, 9). These $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ would oxidize and finally mineralize RhB in the solution, as revealed by Scheme 1. Obviously, the presence of ascorbic acid could relieve the accumulation of ferric ions (Fe(III)) by reductive accelerating the Fe(III)/Fe(II) cycling (Eqs. 10-11), as well as lower the redox potential of Fe(III)/Fe(II) through chelating effect (Eqs. 5, 12), leading to enhanced ROS generation for promoting RhB degradation in the near-neutral solution.

3.4. Denitrification and degradation intermediates detection of RhB.

Ion chromatograph was further used to monitor the NO_3^- releasing after 6 hours' degradation of RhB in the AA/Fe(II)/Air system. In the degradation process, the concentration of NO_3^- was gradually increased to $4.92 \mu\text{mol L}^{-1}$, corresponding to 23.7% of **nitrogen mineralization** (Figure 9). Subsequently, we investigated the degradation pathways of RhB in the AA/Fe(II)/Air system by detection the degradation intermediates of RhB with gas chromatography-mass spectrometry (GC-MS). These identified intermediates included 2-(2,5-dihydroxyphenyl) acetic acid, 2,6-dihydroxybenzoic acid, 2-hydroxybenzoic acid, malonic acid, 2-hydroxypropanoic acid, 2-oxopropanoic acid, 2-hydroxyacetic acid and acetic acid, which confirmed the oxidation degradation of RhB in the AA/Fe(II)/Air system. The structural formulas, names and mass spectra of the RhB degradation intermediates detected by GC-MS were described in the Figure 10. On the basis of the detected intermediates, we inferred a probably oxidation degradation way of RhB. Normally, N-deethylation and destruction of chromophores happened in the first step of RhB degradation. Then opening-ring would occur and be followed with mineralization (Scheme 2).

4. Conclusions

In this study, we developed a ascorbic acid enhanced molecular oxygen activation by Fe(II) to degrade RhB. The presence of ascorbic acid could relieve the accumulation of ferric ions (Fe(III)) by reductive accelerating the Fe(III)/Fe(II) cycling, as well as lower the redox potential of Fe(III)/Fe(II) through chelating effect, leading to enhanced ROS generation for promoting RhB degradation. The developed AA/Fe(II)/Air system provides insight into the aerobic Fe(II) oxidation as well as a green method for effective remediation of organic pollutants.

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Figure Captions

Figure 1. (a) The temporal concentration change of RhB as a function of reaction time in different aerobic processes; (b) plots of $-\ln(C/C_0)$ versus time. The initial concentrations of AA, Fe(II) and RhB were 0.38, 0.1, 0.01 mmol/L, respectively.

Figure 2. (a) The temporal concentration change of RhB as a function of reaction time in the aerobic AA/Fe(II)/Air process with different AA dosages; (b) plots of $-\ln(C/C_0)$ versus time.

Figure 3. (a) Aerobic (Air) and anaerobic (Ar) degradation of RhB. (b) The temporal TOC change of RhB as a function of reaction time during the aerobic degradation over the AA/Fe(II)/Air system (inset was the UV-vis absorption spectra of reaction mixtures).

Figure 4. (a) Time profile of the fluorescence signal of H_2O_2 , and (b) time profile of production of 2-hydroxyterephthalic acid ($\cdot OH$) in the aerobic processes.

Figure 5. Aerobic degradation of RhB in the AA/Fe(II)/Air system in the presence of *iso*-propanol, superoxide dismutase (SOD), and catalase.

Figure 6. (a) The temporal pH values changes of RhB solution as a function of reaction time. (b) The temporal RhB concentration changes as a function of reaction time in Fe(II)/Air, H_2SO_4 /Fe(II)/Air, and AA/Fe(II)/Air systems.

Figure 7. Time profiles of the concentrations for dissolved ferrous ions and total iron in the AA/Fe(II)/Air system.

Figure 8. (a) Comparison of aerobic degradation of RhB in the presence of different ligands; (b) C-V curves in the Fe(II)/Air and the AA/Fe(II)/Air systems.

Figure 9. Concentration change of NO_3^- during RhB degradation in the AA/Fe(II)/Air system.

Figure 10. The total ion chromatography of the reaction mixture and the names, structural formulas and mass spectra of the RhB degradation intermediates detected by GC-MS.

Scheme 1. Schematic illustration for the possible reactive oxygen species generation mechanism during the RhB degradation in the AA/Fe(II)/Air system.

Scheme 2. Possible RhB degradation pathway in the AA/Fe(II)/Air system.

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Scheme 2. Possible RhB degradation pathway in the AA/Fe(II)/Air system.

Graphical Abstract