Ascorbic acid/Fe⁰ composites as an effective persulfate activator for improving the degradation of rhodamine B

Xiangyu Wang,a,c Yi Du,a Huiling Liub and Jun Mab

An ascorbic acid/Fe⁰ composite (H₂A/Fe⁰)-activated persulfate (PS) process was provided for rhodamine B (RhB) removal. Experimental results demonstrated that the H₂A/Fe⁰–PS system exhibits a rapid and continuous oxidation of organic contaminants, and shows great advantages over the conventional Fe⁰–PS system by significantly improving removal efficiency. This H₂A induced dramatic enhancement for RhB degradation could be attributed to both the reduction and chelating ability of H₂A. The H₂A/Fe⁰ composites were characterized using TEM, FE-SEM, FTIR and XPS, indicating that the obtained H₂A/Fe⁰ composites were prepared successfully. Key factors affecting the treatment were determined for the H₂A/Fe⁰–PS system, including H₂A/Fe⁰ dosage, PS dosage, initial solution pH and temperature. Moreover, radical quenching tests revealed that sulfate radicals (SO₄²⁻) and superoxide radicals (O₂⁻) were generated in the H₂A/Fe⁰–PS system, and SO₄²⁻ was the main radical species responsible for RhB degradation. Finally, possible degradation pathways are proposed. These findings prove that the H₂A/Fe⁰–PS system may provide a simple and effective technology for improving the degradation of refractory organic pollutants.

1. Introduction

Nowadays, advanced oxidation processes (AOPs) are regarded as good alternatives for the in situ oxidation of various organic pollutants. In particular, sulfate radical (SO₄²⁻, E₀ = 2.5–3.1 V) based AOPs have become hot topics of research due to their high oxidizing ability, wide pH range and long lifetime. The highly reactive SO₄²⁻ can be generated by activation of persulfate (PS) with heat, UV, metal oxides (Fe₂O₃, CuFe₂O₄), or transition metals (e.g., Fe³⁺, Co³⁺, Cu²⁺). Among these methods, Fe²⁺ has been commonly selected as the activator for PS to generate SO₄²⁻ via eqn (1) due to its non-toxicity, low cost and abundance. However, in the Fe²⁺/PS system, Fe²⁺ is hard to regenerate after conversion to Fe³⁺. In addition, excess Fe²⁺ will scavenge the generated SO₄²⁻ via eqn (2), resulting in reduced degradation efficiency for target contaminants.

\[
\text{S}_2\text{O}_8^{2-} + \text{Fe}^{2+} \rightarrow \text{SO}_4^{2-} + \text{Fe}^{3+} + \text{SO}_2\text{O}_4^{2-} \quad (1)
\]

\[
\text{SO}_4^{2-} + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{SO}_2\text{O}_4^{2-} \quad (2)
\]

Zero-valent iron (Fe⁰) can be an alternative source of Fe²⁺ by gradually releasing Fe²⁺ into an aqueous solution so that Fe²⁺ induced scavenging is minimal. Moreover, in the Fe⁰/PS system, Fe⁰ can not only lessen the generation of ferric hydroxides by recycling Fe³⁺ at the surface of ZVI via eqn (3), but also directly transfer electrons to PS, resulting in the generation of SO₄²⁻ via eqn (4). Peluffo et al. reported that the Fe⁰/PS process yielded a higher removal rate of PAHs than the Fe²⁺–PS process under optimal conditions.

\[
\text{Fe}^{3+} + \text{Fe}^0 \rightarrow \text{Fe}^{2+} \quad (3)
\]

\[
\text{S}_2\text{O}_8^{2-} + \text{Fe}^0 \rightarrow 2\text{SO}_4^{2-} + \text{Fe}^{2+} + 2\text{SO}_2\text{O}_4^{2-} \quad (4)
\]

Recently, an Fe⁰–PS system has been employed to remove various organic pollutants, such as trichloroethylene (TCE), orange G (OG), and bentazon (BTZ). However, the biggest drawback of this technology is that it requires high concentrations of PS and Fe⁰ dosages to achieve favorable activation performance, resulting in increased treatment cost and extra disposal, which may be due to the slow conversion from Fe³⁺ to Fe²⁺. Therefore, accelerating the redox cycle of Fe³⁺/Fe²⁺ is crucial to improving the oxygen activation performance of the Fe⁰–PS system for practical application.

To solve the above-mentioned problems, we conducted a new attempt to provide a novel ascorbic acid/Fe⁰–PS system to degrade organic pollutants in an aqueous system. In this research work, Fe⁰/Fe²⁺ cycles were successfully promoted by employing a reducing agent, ascorbic acid (C₆H₈O₆, H₂A), in the Fe⁰–PS system. Ascorbic acid (H₂A), which is also known as...
vitamin C, is an eco-friendly reducing agent and a natural antioxidant. H₂A has shown great promise in water and wastewater treatment.⁶ Many high oxidation states like H₂O₂, Fe³⁺, and Cr⁶⁺ could be reduced using H₂A as an electron donor.¹⁷,¹⁸ Fukuchi et al. reported that the dosages of H₂O₂ and Fe⁢²⁺ could be largely reduced with the addition of H₂A into traditional Fenton-like processes, leading to a relatively steady Fe⁢²⁺ concentration and higher production of free radicals.¹⁹ In addition, H₂A is a bidentate ligand with a bifunctional enediol group that has the ability to solubilize metal ions by chelate formation.²⁰ Therefore, it might be reasonable to introduce H₂A into the Fe⁢²⁺-PS system to improve the degradation efficiency for pollutants. Although it has also been reported that Fe⁢⁰ nanoparticles can be stabilized with ascorbic acid to increase the durability of synthesized Fe⁢⁰,²¹ To the best of our knowledge, the use of H₂A coated Fe⁢⁰ nanoparticles as an activator to enhance the activation performance of PS has not been reported so far.

To investigate the degradation efficiency of the H₂A/Fe⁰–PS system, rhodamine B (RhB) was selected as a model pollutant because it is an extremely stable and resistant aromatic group that has the ability to solubilize metal ions by chelate formation.²² Therefore, it might be reasonable to introduce H₂A into the Fe⁢²⁺-PS system to improve the degradation efficiency for pollutants. Although it has also been reported that Fe⁢⁰ nanoparticles can be stabilized with ascorbic acid to increase the durability of synthesized Fe⁢⁰,²¹ To the best of our knowledge, the use of H₂A coated Fe⁰ nanoparticles as an activator to enhance the activation performance of PS has not been reported so far.

To investigate the degradation efficiency of the H₂A/Fe⁰–PS system, rhodamine B (RhB) was selected as a model pollutant because it is an extremely stable and resistant aromatic compound, and hard to degrade using conventional wastewater treatment methods. The additional purposes of this study were to (1) investigate the degradation performance of RhB in the H₂A/Fe⁰–PS system; (2) explore the mechanism of enhanced RhB degradation in the H₂A/Fe⁰–PS system; and (3) reveal the important parameters (H₂A/Fe⁰ dosage, PS dosage, pH and temperature) affecting the H₂A/Fe⁰–PS system.

2. Materials and methods

2.1. Chemicals and materials

Potassium borohydride (KBH₄, 99%), ferrous sulfate heptahydrate (FeSO₄·7H₂O), sodium persulfate (Na₂S₂O₈), sodium hydroxide (NaOH, 99%), rhodamine B (RhB), sulfuric acid (H₂SO₄, 95% to 98%), sodium acetate anhydrous (CH₃COONa), ethanol, 1,10-phenanthroline (C₁₂H₈N₂), tert-butyl alcohol (TBA), methanol (MeOH), 1,4-benzoquinone (BQ), acetone and ascorbic acid (H₂A) were prepared with deionized water before each run.

2.2. Synthesis of H₂A/Fe⁰

The H₂A/Fe⁰ was synthesized in an anaerobic glove box under the protection of purified N₂. First, a 0.5 M solution of Fe⁢³⁺ was prepared by dissolving FeSO₄·7H₂O in deionized water (100 mL). Then, a certain volume stabilizer (H₂A, 10 g L⁻¹) solution was added into the FeSO₄ solution with electromagnetic stirring for 15 min. After intensive mixing, 100 mL of 1.5 M of KBH₄ solution was added dropwise into the mixture solution. After delivering all of the KBH₄ solution, the solution was stirred continuously for 30 min. Subsequently, the solid precipitation was filtered with a 0.45 μm membrane filter under vacuum, followed by rinsing with deionized water, absolute ethanol, and acetone alternately 3 times.

2.3. Experimental procedures

Degradation experiments were carried out in 250 mL serum bottles, which were filled with 50 mL of RhB solution. A predetermined amount of PS was quickly added into the pH-adjusted RhB solution. Subsequently, a certain amount of H₂A/Fe⁰ was quickly added into the above solution to trigger the reaction. The initial pH value of the solution was adjusted with NaOH (0.1 M) or H₂SO₄ (0.1 M). The bottles were then placed into a temperature-controlled orbital shaker with a constant shaking speed (170 rpm) to ensure a complete mixing state. At predetermined time intervals, solution samples were taken using disposable syringes, and then filtered with a 0.45 μm filter membrane. Subsequently, the filtered sample was mixed with excess methanol (v/v = 1 : 1) to quench the reaction before analysis.

The concentration of RhB was determined with a UV-2450 visible spectrophotometer (Shimadzu, Japan), and its maximum characteristic wavelength was adopted at 554 nm. The concentrations of total iron and ferrous ions were determined according to the 1,10-phenanthroline colorimetric method.²³ Radical scavenging tests were conducted and three radical scavengers, MeOH, TBA and BQ, were used to determine the type of the predominant reactive oxygen species for RhB degradation.

2.4. Characterizations

The morphology and particle structure of H₂A/Fe⁰ and Fe⁰ were studied with a high-resolution field emission scanning electron microscope (FE-SEM, JEOL Ltd., Japan) at an accelerating voltage of 5.0 kV with an X-ray energy-dispersive spectroscopy (EDS) detector (IE300X, Oxford, United Kingdom) and transmission electron microscopy (TEM, JEOL Ltd., Japan). The surface chemical structure and composition of the H₂A/Fe⁰ and Fe⁰ particles were studied by Fourier transform infrared spectroscopy (FTIR, Perkin-Elmer Instrument Co., Ltd., USA). The element valence and chemical groups of H₂A/Fe⁰ and Fe⁰ were determined by X-ray photoelectron spectroscopy using monochromatic Mg Kα radiation (XPS, Model PHI 5700, Physical Electronics, USA).

3. Results and discussion

3.1. Comparison of RhB degradation in different systems

Comparative experiments were carried out in different systems to determine the effects of the synthesized H₂A/Fe⁰ particles on PS activation for RhB degradation under the same operating conditions. As shown in Fig. 1a, about 35.28% RhB was removed by Fe⁰ alone, and only 31.33% RhB was removed by H₂A/Fe⁰ within 90 min, indicating that some of the reactive sites might be blocked by the excessive dispersant coated on the Fe⁰ surfaces. The removal efficiency for RhB was apparently improved when the reaction time was prolonged, mainly because of desorption of H₂A into the aqueous solution. In contrast, PS alone could degrade 54.59% of RhB within 90 min. The carboxyl and phenyl groups of RhB might be capable of PS activation.²⁴ In addition, activation of PS by Fe⁰ was also
investigated, and the results showed that approximately 18% of the RhB was removed over 60 min in the Fe0/PS system. A slightly improved removal efficiency of RhB was achieved in the H2A/PS system because H2A can react with PS to generate SO42- and CO2, according to eqn (5) and (6).

However, more than 90% of the RhB was removed with H2A/Fe0 activated PS. Therefore, the high activity of the H2A/Fe0 composites for PS activation was assumed to be the result of the existence of a synergistic effect in this system.

\[
\begin{align*}
H_2A + S_2O_8^{2-} & \rightarrow 2H^+ + SO_4^{2-} + SO_4^{2-} + A^{-} \quad (5) \\
HA^- + S_2O_8^{2-} & \rightarrow H^+ + SO_4^{2-} + SO_4^{2-} + A^- \quad (6)
\end{align*}
\]

The reactivity of H2A/Fe0 particles with different H2A content was further investigated. As shown in Fig. 1b, the highest removal efficiency was achieved with an H2A solution addition amount of 3.60%wt (to Fe2+) during the synthesis process of Fe0. For an H2A addition content higher than 3.60%, the excess H2A might occupy the available reactive sites of Fe0 particles and then block the target pollutants diffusing onto the surface sites. In contrast, insufficient loading of the coating onto the surface of Fe0 might result in ineffective dispersion of the Fe0, indicating that the optimal H2A concentration would be 3.60%.

Therefore, 3.60% was selected in the following characterization and degradation experiments.

3.2. Characterization of H2A/Fe0

The morphology of the Fe0 and H2A/Fe0 was observed by TEM and FE-SEM. The TEM observation (Fig. 2a) on the Fe0 shows that bare Fe0 particles were aggregated and featured as a necklace-like chain of length 80–100 nm. When H2A was added, the dispersion of Fe0 was significantly increased (Fig. 2b), indicating that H2A could act as a dispersant for Fe0 nanoparticles. The particle size of H2A/Fe0 ranges from 20 to 80 nm. The reason might be that the added H2A could coordinate with ferrous ions to indirectly control the growth of iron particles, resulting in the smaller size of the H2A/Fe composite.

Fig. 2c shows the representative FE-SEM image of the as-synthesized bare Fe0, which exhibits a spherical morphology with a size in the range 80–100 nm, and which tends to aggregate together due to the magnetic interactions between iron particles. Comparatively, with the coating of H2A, it can be observed that the H2A/Fe0 had a smaller size than bare Fe0 (Fig. 2d). Simultaneously, the EDS spectrum further revealed the successful incorporation of H2A and iron nanoparticles (Fig. 3e).

In order to prove the existence of functional groups of H2A on the surface of the Fe nanoparticles, Fe0 and H2A/Fe0 were analyzed by FTIR spectroscopy. As shown in Fig. 3, the absorption peak on H2A/Fe0 at about 3417 cm⁻¹ was significantly larger than that on Fe0, which was attributed mainly to stretching vibrations of –OH. In addition, compared with the
spectrum of Fe\textsuperscript{0}, there are several inconspicuous infrared characteristic peaks for H\textsubscript{2}A/Fe\textsuperscript{0}, among which the absorption peak appearing at approximately 2925 cm\textsuperscript{-1} was assigned to \textendash \text{CH}. The bands at 1328.7 cm\textsuperscript{-1} are attributed to C\textendash O vibrations. Meanwhile, an additional adsorption peak at 1629 cm\textsuperscript{-1} corresponded to the stretching vibrations of C\textendash C groups, indicating the presence of the \text{H}_2\text{A} constituent.\textsuperscript{15}

XPS was used to investigate the composition and chemical state of Fe\textsuperscript{0} before and after coating by H\textsubscript{2}A. The full-range survey spectra of Fe\textsuperscript{0} and H\textsubscript{2}A/Fe\textsuperscript{0} particles are illustrated in Fig. 4a, showing that the nanoparticle surface consists mainly of iron (Fe), oxygen (O), and carbon (C). The small amount of carbon appearing in the Fe\textsuperscript{0} spectrum is likely to be attributed to carbon dioxide, water, and/or organic compounds (such as ethanol and acetone) during the fabrication, drying and preserving processes.\textsuperscript{26} Detailed XPS patterns for the C 1s regions of the Fe\textsuperscript{0} and H\textsubscript{2}A/Fe\textsuperscript{0} particles are presented in Fig. 4b and c. Compared with Fe\textsuperscript{0}, a conspicuous peak at 284.7 eV appeared in the spectrum of H\textsubscript{2}A/Fe\textsuperscript{0}, corresponding to C\textendash C species, verifying the presence of \text{H}_2\text{A}. All the above characterization results of FTIR and XPS confirmed that H\textsubscript{2}A had been successfully coated onto Fe\textsuperscript{0}.

### 3.3. Factors affecting RhB degradation in the H\textsubscript{2}A/Fe\textsuperscript{0}–PS system

The effects of PS dosage, H\textsubscript{2}A/Fe\textsuperscript{0} dosage, pH value, and temperature on RhB degradation were investigated and the results are shown in Fig. 5. Fig. 5a shows the effect of PS dosage on RhB degradation. The results clearly show that the degradation of RhB accelerated as the PS dosage increased from 0.1 to 0.3 g L\textsuperscript{-1}. Since PS was the SO\textsubscript{4}\textsuperscript{2–} donor, a higher PS dosage would improve the formation of SO\textsubscript{4}\textsuperscript{2–}. However, when the PS dosage was further increased to 0.5 g L\textsuperscript{-1}, it led to a decline in RhB degradation efficiency. Similar results were also reported in other studies.\textsuperscript{27} A reasonable explanation for this phenomenon is that the excess S\textsubscript{2}O\textsubscript{8}\textsuperscript{2–} may lead to SO\textsubscript{4}\textsuperscript{2–} scavenging (eqn (7)) and the reaction between two SO\textsubscript{4}\textsuperscript{2–} (eqn (8)).\textsuperscript{28} Hence, 0.3 g L\textsuperscript{-1} PS was selected as the optimal dosage in the following experiments.

**\text{SO}_4^{2–} + S_2\text{O}_8^{2–} \rightarrow \text{SO}_4^{2–} + S_2\text{O}_6^{4–} \quad (7)**

**\text{SO}_4^{2–} + \text{SO}_4^{2–} \rightarrow S_2\text{O}_6^{4–} \quad (8)**

The effect of H\textsubscript{2}A/Fe\textsuperscript{0} dosage on RhB degradation was evaluated with the H\textsubscript{2}A/Fe\textsuperscript{0} dosage ranging from 0.15 to 0.60 g L\textsuperscript{-1}. As shown in Fig. 5b, the increase in the activator dosage significantly promoted the degradation of RhB, which may be because the increase in H\textsubscript{2}A/Fe\textsuperscript{0} dosage could provide more
neutral and alkaline conditions. which suggested that the degradation rate was lowered under contaminants.
P pH value played an important parameter in the degradation of acidic and weakly alkaline conditions were benefited.

The better performance under acidic conditions in the present study may be because: (1) At lower pH values, the Fe(0) corrosion rate could be accelerated, leading to much faster release of Fe(2+)
which favors the induction of eqn (1) to produce more SO4$^{2-}$. (2) At a pH higher than 7, the formation of Fe(2+) complexes could inhibit PS activation by eqn (9). Also, the reactions between SO4$^{2-}$ and H2O/OH$^-$ could result in the rapid decay of SO4$^{2-}$ (eqn (10) and (11)). Overall, acidic and weakly alkaline conditions were beneficial for RhB destruction. Compared with the Fenton process that must be carried out over a narrow pH range, the results suggested that the novel method we provide in this research possesses tremendous advantages for applications in practice.

$$\text{Fe}^{2+} + \text{H}_2\text{O} \rightarrow \text{FeOH}^+ + \text{H}^+$$ \hspace{1cm} (9)

All pH: $\text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{SO}_4^{2-} + \text{H}^+$ \hspace{1cm} (10)

Alkaline pH: $\text{SO}_4^{2-} + \text{OH}^- \rightarrow \cdot\text{OH} + \text{SO}_4^{2-}$ \hspace{1cm} (11)

The degradation reaction of RhB was also found to be influenced by solution temperature. As shown in Fig. 5d, higher temperatures favored the degradation of RhB by PS activated with H2A/Fe0, which could be associated with the thermal activation of PS to generate free radicals [eqn (12)], as well as the acceleration of the reaction between H2A/Fe0 and PS, probably because the diffusion and mobility of RhB molecules increased.

$$\text{S}_2\text{O}_8^{2-} + \text{heat} \rightarrow \text{SO}_4^{2-}$$ \hspace{1cm} (12)

3.4. Degradation mechanism

3.4.1 Identification of free radicals in the H2A/Fe0–PS system. It has been reported that a series of reactive oxygen species, e.g., SO4$^{2-}$, OH and superoxide anion radicals (O2$^-\cdot$), were generated in a PS/Fe(II)/hydroxylamine (HA) system and may also be generated in the H2A/Fe0–PS system. In order to evaluate the major radical species for the RhB oxidation reaction, scavenging experiments were performed in the H2A/Fe0–PS system by adding MeOH, TBA and BQ into the reaction solution. MeOH (with $\alpha$-hydrogen) is an effective quencher for both $\cdot$OH (1.2 x 10$^8$ to 2.8 x 10$^9$ M$^{-1}$ s$^{-1}$) and SO4$^{2-}$ (1.6 x 10$^7$ to 7.7 x 10$^7$ M$^{-1}$ s$^{-1}$). In contrast, TBA (without $\alpha$-hydrogen) has an approximately 1000 times greater rate constant with $\cdot$OH (3.8 x 10$^8$ to 7.6 x 10$^8$ M$^{-1}$ s$^{-1}$) than with SO4$^{2-}$ (4.0 x 10$^5$ to 9.1 x 10$^5$ M$^{-1}$ s$^{-1}$). Therefore, MeOH was used to scavenge both radicals, and TBA was used to selectively scavenge $\cdot$OH. Moreover, we used BQ as an effective scavenger of O2$^-\cdot$ by electron transfer to generate benzoquinone radicals.

As shown in Fig. 6, 94.78% of RhB was degraded in 30 min when no quenching agent was added. However, with the addition of BQ and TBA, the removal efficiency of RhB decreased to 82.44% and 64.63% in 30 min, respectively. Meanwhile, the degradation of RhB was almost completely inhibited (27.98%) by the addition of MeOH. These data indicate that O2$^-\cdot$, SO4$^{2-}$ and $\cdot$OH are generated in the H2A/Fe0–PS system. Similar findings were reported by a previous study. It can be preliminarily inferred that O2$^-\cdot$ may be derived from catalytic hydrolysis of PS

![Fig. 5 Parameters affecting the degradation of RhB: (a) PS dosage, (b) H2A/Fe0 dosage, (c) pH value, and (d) temperature. Except for the investigated parameter, other parameters were fixed at C0 = 50 mg L$^{-1}$, PS = 0.3 g L$^{-1}$, H2A/Fe0 = 0.3 g L$^{-1}$, pH = 6.50 and T = 298 K.](image)

![Fig. 6 Effect of different radical quenching agents on RhB removal. Reaction conditions: C0 = 50 mg L$^{-1}$, PS = 0.3 g L$^{-1}$, H2A/Fe0 = 0.3 g L$^{-1}$, pH = 6.50 and T = 298 K.](image)
in accordance with eqn (13) and (14). Hence, the scavenging studies clearly prove the simultaneous participation of O$_2$⁻⁻, SO$_4$²⁻ and ‘OH in the H$_2$A/Fe$^0$–PS oxidation process, and SO$_4$²⁻ played a major role in achieving a good oxidation reaction.

\[
\text{S}_2\text{O}_8^{2-} + 2\text{H}_2\text{O} \rightarrow 2\text{SO}_4^{2-} + \text{HO}_2^- + 3\text{H}^+ \quad (13)
\]

\[
\text{S}_2\text{O}_8^{2-} + \text{HO}_2^- \rightarrow \text{SO}_4^{2-} + \text{SO}_4^{2-} + \text{O}_2^- + \text{H}^+ \quad (14)
\]

**3.4.2 UV-vis spectral changes.** The UV-vis spectra were used to observe changes during the degradation of RhB by the H$_2$A/Fe$^0$–PS system at different reaction times. As shown in Fig. 7, there were two main characteristic absorption bands of RhB in the UV region (259 nm) and visible light region (545 nm), respectively. The UV absorbance at 259 nm corresponds to the existence of aromatic rings in RhB. The visible absorbance at 545 nm is responsible for the RhB coloration due to the existence of aromatic rings in RhB. The visible absorbance at 545 nm is responsible for the RhB coloration due to the existence of aromatic rings in RhB. The visible absorbance at 545 nm is responsible for the RhB coloration due to the existence of aromatic rings in RhB.

The decrease in absorbance at 259 nm indicates the decrease in the main chromophore band of RhB, and the absorbance at 554 nm is responsible for the RhB coloration due to the existence of aromatic rings in RhB. The visible absorbance at 545 nm is responsible for the RhB coloration due to the existence of aromatic rings in RhB. The visible absorbance at 545 nm is responsible for the RhB coloration due to the existence of aromatic rings in RhB. The visible absorbance at 545 nm is responsible for the RhB coloration due to the existence of aromatic rings in RhB.

The UV-vis adsorption spectra of RhB, as shown in Fig. 7. Usually for RhB degradation, two possible competitive mechanisms occur, i.e. N-demethylation and cleavage of the chromophore structure. First, the decrease in the main chromophore band of RhB at 545 nm with an increase in the reaction time indicates the destruction of the xanthene structure of the chromophore. Second, the decrease in absorbance at 259 nm indicates the destruction of the aromatic part. Third, some new peaks appeared at around 210 nm and 328 nm, possibly demonstrating the yield of intermediate or final products.

**3.4.3 The role of H$_2$A in enhancing RhB degradation.** The role of H$_2$A on enhancing RhB degradation in the H$_2$A/Fe$^0$–PS system was investigated. First of all, it is generally recognized that H$_2$A is a potent antioxidant agent with the ability to prevent the aggregation of Fe$^0$ by the effect of coating (Fig. 2b and d).

In addition, H$_2$A is a weak acid with the ability to solubilize metal ions by Fe$^{2+}$–H$_2$A (Fe$^{2+}$/H$_2$A) complex (eqn (15)) formation either in solution or on the surface of iron based materials, which can not only further activate PS (eqn (16)) and account for the generation of SO$_4$²⁻, but also react with O$_2$ to produce O$_2$⁻ in accordance with eqn (17). Besides its acidity, H$_2$A can also serve as a reducing agent, which is capable of effectively reducing Fe$^{3+}$ and realizing Fe$^{3+}$/Fe$^{2+}$ redox cycles in the system (eqn (18)).

\[
\text{Fe}^{2+} + \text{H}_2\text{A} \rightarrow \text{Fe}^{3+}\text{H}_2\text{A}_x \quad (15)
\]

\[
\text{Fe}^{2+}\text{H}_2\text{A}_x + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Fe}^{3+}\text{H}_2\text{A}_y + \text{SO}_4^{2-} + \text{SO}_4^{2-} \quad (16)
\]

\[
\text{Fe}^{2+}\text{H}_2\text{A}_x + \text{O}_2 \rightarrow \text{Fe}^{3+}\text{H}_2\text{A}_y + \text{O}_2^- \quad (17)
\]

\[
\text{H}_2\text{A} + 2\text{Fe}^{3+} \rightarrow \text{Fe}^{2+} + \text{A} + 2\text{H}^+ \quad (18)
\]

To confirm this opinion, the changes in concentration of total iron and ferrous iron in the solution were monitored during the oxidation of RhB. Fig. 8 shows that the total iron concentration increased as the reaction time increased, with no period of decline. This phenomenon could be attributed to the continuous leaching of iron from H$_2$A/Fe$^0$. By contrast, the leaching of iron was faster during the oxidation of RhB by the H$_2$A/Fe$^0$ composite than by pristine Fe$^0$ and this result further confirms the pronounced weak acid effect of H$_2$A with the ability to solubilize metal ions. Moreover, the ferrous iron concentration was found to increase from 22.32 to 29.11 mg L$^{-1}$ in the first 20 min, and then remained relatively stable over the later reaction time without decreasing. This was due to the electron transfer from H$_2$A to both the surface and dissolved Fe$^{3+}$ (via eqn 18) resulting in an effective Fe$^{3+}$/Fe$^{2+}$ cycle. As expected, the reductive effect of H$_2$A was also promoted to form more and more Fe$^{3+}$ and SO$_4$²⁻ in the H$_2$A/Fe$^0$–PS system, which results in an acceleration in RhB degradation.

The H$_2$A/Fe$^0$–PS system exhibits significant superiority for the removal of RhB. Fig. 9 illustrates the proposed conceptual model of the RhB removal process by the H$_2$A/Fe$^0$–PS system. The superiority of the H$_2$A/Fe$^0$–PS system is mainly attributed to: (1) H$_2$A can reduce the structure size of Fe$^0$ particles and increase their dispersibility; however, considering that the aggregation of H$_2$A/Fe$^0$ was still remarkable (Fig. 2b and d), we...
believe that the high activation performance of H2A/Fe0 was not mainly due to the increased dispersibility in solution. (2) H2A is a weak acid that has the ability to solubilize metal ions by Fe2+/H2A complex formation, resulting in another pathway for the production of O2− by eqn (17), which is helpful for improving the degradation. (3) H2A can also serve as a reducing agent, and the presence of H2A accelerated the redox cycle of Fe3+/Fe2+ and robust Fe2+ regeneration to promote RhB degradation. Therefore, this H2A/Fe0–PS system can produce more SO4− and O2− than the Fe0–PS system alone. In a word, the H2A/Fe0–PS system involved the generation of 'OH, SO4− and O2− species, among which SO4− played a key role in the degradation of RhB.

4. Conclusions

In this study, we present H2A/Fe0 nanoparticles as a heterogeneous PS activator for the effective degradation of RhB. The physical-chemical properties of H2A/Fe0 nanoparticles were characterized by TEM, FE-SEM, FTIR and XPS. Compared with bare Fe0, the H2A/Fe0 composites showed much higher performance for PS activation for RhB degradation. We explored the role of H2A and concluded that both its reduction and chelating ability contribute to the good performance of the H2A/Fe0–PS system. In addition, the radical scavenging tests clearly confirmed the generation of SO4−, 'OH and O2− and that the primary reactive oxygen species is SO4− in the H2A/Fe0–PS system. Batch experiments indicated that the optimal PS dosage is 0.3 g L−1. RhB removal efficiency increased with increasing H2A/Fe0 dosage and solution temperature, and it increased with a decrease in pH values. The findings in this study strongly suggested that the H2A/Fe0 activated PS process is a highly promising technique for the degradation of dye wastewater and other refractory organic toxic pollutants.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors gratefully acknowledge the financial support by National Natural Science Foundation of China (NSFC, No. 51368025 and No. 51068011).

References

1. Y. Deng and R. Zhao, Curr. Pollut. Rep., 2015, 1, 167−176.
2. J. Yan, M. Lei, L. Zhu, M. N. Anjum, J. Zou and H. Tang, J. Hazard. Mater., 2011, 186, 1398−1404.
3. Y. Fan, Y. Ji, D. Kong, J. Lu and Q. Zhou, J. Hazard. Mater., 2015, 300, 39−47.
4. J. Y. Fang and C. Shang, Environ. Sci. Technol., 2012, 46, 8976−8983.
5. G.-D. Fang, D. D. Dionysiou, S. R. Al-Abed and D.-M. Zhou, Appl. Catal., B, 2013, 129, 325−332.
6. X. Zhang, M. Feng, R. Qu, H. Liu, L. Wang and Z. Wang, Chem. Eng. J., 2016, 301, 1−11.
7. X. Jiang, Y. Wu, P. Wang, H. Li and W. Dong, Environ. Sci. Pollut. Res. Int., 2013, 20, 4947−4953.
8. C. Wang, J. Wan, Y. Ma and Y. Wang, Res. Chem. Intermed., 2015, 42, 481−497.
9. F. Gong, L. Wang, D. Li, F. Zhou, Y. Yao, W. Lu, S. Huang and W. Chen, Chem. Eng. J., 2015, 267, 102−110.
10. X. Wei, N. Gao, C. Li, Y. Deng, S. Zhou and L. Li, Chem. Eng. J., 2016, 285, 660−670.
11. M. Peluffo, F. Pardo, A. Santos and A. Romero, Sci. Total Environ., 2016, 563−564, 649−656.
12. J. Yan, L. Han, W. Gao, S. Xue and M. Chen, Bioresour. Technol., 2015, 175, 269−274.
13. X. Xiong, B. Sun, J. Zhang, N. Gao, J. Shen, J. Li and X. Guan, Water Res., 2014, 62, 53−62.
14. B. M. Voelker and B. Sulzberger, Environ. Sci. Technol., 1996, 30, 1106−1114.
15. C. Sun, R. Zhou, J. E. J. Sun, Y. Su and H. Ren, RSC Adv., 2016, 6, 10633−10640.
16. Y. T. Lin and C. Liang, Environ. Sci. Technol., 2013, 47, 3299−3307.
17. X. Hou, X. Huang, Z. Ai, J. Zhao and L. Zhang, J. Hazard. Mater., 2016, 310, 170−178.
18. X.-R. Xu, H.-B. Li, X.-Y. Li and J.-D. Gu, Chemosphere, 2004, 57, 609−613.
19. S. Fukuchi, R. Nishimoto, M. Fukushima and Q. Zhu, Appl. Catal., B, 2014, 147, 411−419.
20. Y.-T. Lin, C. Liang and C.-W. Yu, Ind. Eng. Chem. Res., 2016, 55, 2302−2308.
21. M. Savasari, M. Emadi, M. A. Bahmanyar and P. Biparva, J. Ind. Eng. Chem., 2015, 21, 1403−1409.
22. Z.-H. Diao, X.-R. Xu, D. Jiang, L.-J. Kong, Y.-X. Sun, Y.-X. Hu, Q.-W. Hao and H. Chen, Chem. Eng. J., 2016, 302, 213−222.
23. J. Du, J. Bao, X. Fu, C. Lu and S. H. Kim, Sep. Purif. Technol., 2016, 163, 145−152.
24. Y. Lei, H. Zhang, J. Wang and J. Ai, Chem. Eng. J., 2015, 270, 73−79.
25. X. Wang, Y. Du and J. Ma, Appl. Surf. Sci., 2016, 390, 50−59.
26. X. Wang, P. Wang, J. Ma, H. Liu and P. Ning, Appl. Surf. Sci., 2015, 345, 57−66.
27. H. Chen, Z. Zhang, M. Feng, W. Liu, W. Wang, Q. Yang and Y. Hu, Chem. Eng. J., 2017, 313, 498−507.
28. L. Hou, H. Zhang and X. Xue, Sep. Purif. Technol., 2012, 84, 147−152.
29. C. Tan, N. Gao, W. Chu, C. Li and M. R. Templeton, *Sep. Purif. Technol.*, 2012, 95, 44–48.
30. Y. Leng, W. Guo, X. Shi, Y. Li and L. Xing, *Ind. Eng. Chem. Res.*, 2013, 52, 13607–13612.
31. J. Li, Q. Liu, Q. Q. Ji and B. Lai, *Appl. Catal., B*, 2017, 200, 633–646.
32. C. Tan, N. Gao, Y. Deng, N. An and J. Deng, *Chem. Eng. J.*, 2012, 203, 294–300.
33. X. Wu, X. Gu, S. Lu, Z. Qiu, Q. Sui, X. Zang, Z. Miao and M. Xu, *Sep. Purif. Technol.*, 2015, 147, 186–193.
34. A. Farhat, J. Keller, S. Tait and J. Radjenovic, *Environ. Sci. Technol.*, 2015, 49, 14326–14333.
35. R. Kumar, E. H. Gleissner, E. G. Tiu and Y. Yamakoshi, *Org. Lett.*, 2016, 18, 184–187.
36. Y. Xu, J. Ai and H. Zhang, *J. Hazard. Mater.*, 2016, 309, 87–96.
37. J. Hong, S. Lu, C. Zhang, S. Qi and Y. Wang, *Chemosphere*, 2011, 84, 1542–1547.
38. M. F. Hou, L. Liao, W. D. Zhang, X. Y. Tang, H. F. Wan and G. C. Yin, *Chemosphere*, 2011, 83, 1279–1283.
39. K. P. Mishra and P. R. Gogate, *Sep. Purif. Technol.*, 2010, 75, 385–391.
40. X. Hou, W. Shen, X. Huang, Z. Ai and L. Zhang, *J. Hazard. Mater.*, 2016, 308, 67–74.