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# Ascorbic acid/ $\text{Fe}^0$ composites as an effective persulfate activator for improving the degradation of rhodamine B

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An ascorbic acid/ $\text{Fe}^0$  composite ( $\text{H}_2\text{A}/\text{Fe}^0$ )-activated persulfate (PS) process was provided for rhodamine B (RhB) removal. Experimental results demonstrated that the  $\text{H}_2\text{A}/\text{Fe}^0$ -PS system exhibits a rapid and continuous oxidation of organic contaminants, and shows great advantages over the conventional  $\text{Fe}^0$ -PS system by significantly improving removal efficiency. This  $\text{H}_2\text{A}$  induced dramatic enhancement for RhB degradation could be attributed to both the reduction and chelating ability of  $\text{H}_2\text{A}$ . The  $\text{H}_2\text{A}/\text{Fe}^0$  composites were characterized using TEM, FE-SEM, FTIR and XPS, indicating that the obtained  $\text{H}_2\text{A}/\text{Fe}^0$  composites were prepared successfully. Key factors affecting the treatment were determined for the  $\text{H}_2\text{A}/\text{Fe}^0$ -PS system, including  $\text{H}_2\text{A}/\text{Fe}^0$  dosage, PS dosage, initial solution pH and temperature. Moreover, radical quenching tests revealed that sulfate radicals ( $\text{SO}_4^{\cdot-}$ ), hydroxyl radicals ( $^{\cdot}\text{OH}$ ) and superoxide radicals ( $\text{O}_2^{\cdot-}$ ) were generated in the  $\text{H}_2\text{A}/\text{Fe}^0$ -PS system, and  $\text{SO}_4^{\cdot-}$  was the main radical species responsible for RhB degradation. Finally, possible degradation pathways are proposed. These findings prove that the  $\text{H}_2\text{A}/\text{Fe}^0$ -PS system may provide a simple and effective technology for improving the degradation of refractory organic pollutants.

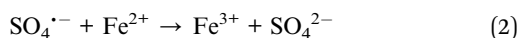
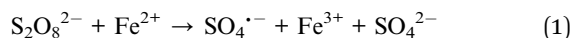
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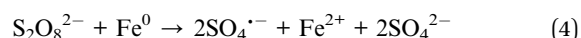
## 1. Introduction

Nowadays, advanced oxidation processes (AOPs) are regarded as good alternatives for the *in situ* oxidation of various organic pollutants.<sup>1</sup> In particular, sulfate radical ( $\text{SO}_4^{\cdot-}$ ,  $E_0 = 2.5\text{--}3.1$  V) based AOPs have become hot topics of research due to their high oxidizing ability, wide pH range and long lifetime.<sup>2</sup> The highly reactive  $\text{SO}_4^{\cdot-}$  can be generated by activation of persulfate (PS) with heat,<sup>3</sup> UV,<sup>4</sup> metal oxides ( $\text{Fe}_3\text{O}_4$ ,  $\text{CuFe}_2\text{O}_4$ ),<sup>5,6</sup> or transition metals (e.g.,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ).<sup>7,8</sup> Among these methods,  $\text{Fe}^{2+}$  has been commonly selected as the activator for PS to generate  $\text{SO}_4^{\cdot-}$  via eqn (1) due to its non-toxicity, low cost and abundance.<sup>9</sup> However, in the  $\text{Fe}^{2+}$ /PS system,  $\text{Fe}^{2+}$  is hard to regenerate after conversion to  $\text{Fe}^{3+}$ . In addition, excess  $\text{Fe}^{2+}$  will scavenge the generated  $\text{SO}_4^{\cdot-}$  via eqn (2), resulting in reduced degradation efficiency for target contaminants.



Zero-valent iron ( $\text{Fe}^0$ ) can be an alternative source of  $\text{Fe}^{2+}$  by gradually releasing  $\text{Fe}^{2+}$  into an aqueous solution so that  $\text{Fe}^{2+}$

induced scavenging is minimal.<sup>10</sup> Moreover, in the  $\text{Fe}^0$ /PS system,  $\text{Fe}^0$  can not only lessen the generation of ferric hydroxides by recycling  $\text{Fe}^{3+}$  at the surface of ZVI via eqn (3), but also directly transfer electrons to PS, resulting in the generation of  $\text{SO}_4^{\cdot-}$  via eqn (4). Peluffo *et al.* reported that the  $\text{Fe}^0$ /PS process yielded a higher removal rate of PAHs than the  $\text{Fe}^{2+}$ -PS process under optimal conditions.<sup>11</sup>



Recently, an  $\text{Fe}^0$ -PS system has been employed to remove various organic pollutants, such as trichloroethylene (TCE),<sup>12</sup> orange G (OG),<sup>13</sup> and bentazon (BTZ).<sup>10</sup> However, the biggest drawback of this technology is that it requires high concentrations of PS and  $\text{Fe}^0$  dosages to achieve favorable activation performance, resulting in increased treatment cost and extra disposal,<sup>14</sup> which may be due to the slow conversion from  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ .<sup>15</sup> Therefore, accelerating the redox cycle of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  is crucial to improving the oxygen activation performance of the  $\text{Fe}^0$ -PS system for practical application.

To solve the above-mentioned problems, we conducted a new attempt to provide a novel ascorbic acid/ $\text{Fe}^0$ -PS system to degrade organic pollutants in an aqueous system. In this research work,  $\text{Fe}^{3+}/\text{Fe}^{2+}$  cycles were successfully promoted by employing a reducing agent, ascorbic acid ( $\text{C}_6\text{H}_8\text{O}_6$ ,  $\text{H}_2\text{A}$ ), in the  $\text{Fe}^0$ -PS system. Ascorbic acid ( $\text{H}_2\text{A}$ ), which is also known as

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vitamin C, is an eco-friendly reducing agent and a natural antioxidant.  $H_2A$  has shown great promise in water and wastewater treatment.<sup>16</sup> Many high oxidation states like  $H_2O_2$ ,  $Fe^{3+}$ , and  $Cr^{6+}$  could be reduced using  $H_2A$  as an electron donor.<sup>17,18</sup> Fukuchi *et al.* reported that the dosages of  $H_2O_2$  and  $Fe^{2+}$  could be largely reduced with the addition of  $H_2A$  into traditional Fenton-like processes, leading to a relatively steady  $Fe^{2+}$  concentration and higher production of free radicals.<sup>19</sup> In addition,  $H_2A$  is a bidentate ligand with a bifunctional enediol group that has the ability to solubilize metal ions by chelate formation.<sup>20</sup> Therefore, it might be reasonable to introduce  $H_2A$  into the  $Fe^0$ -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  $Fe^0$ .<sup>21</sup> To the best of our knowledge, the use of  $H_2A$  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  $H_2A/Fe^0$ -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  $H_2A/Fe^0$ -PS system; (2) explore the mechanism of enhanced RhB degradation in the  $H_2A/Fe^0$ -PS system; and (3) reveal the important parameters ( $H_2A/Fe^0$  dosage, PS dosage, pH and temperature) affecting the  $H_2A/Fe^0$ -PS system.

## 2. Materials and methods

### 2.1. Chemicals and materials

Potassium borohydride ( $KBH_4$ , 99%), ferrous sulfate heptahydrate ( $FeSO_4 \cdot 7H_2O$ ), sodium persulfate ( $Na_2S_2O_8$ ), sodium hydroxide (NaOH, 99%), rhodamine B (RhB), sulfuric acid ( $H_2SO_4$ , 95% to 98%), sodium acetate anhydrous ( $CH_3COONa$ ), ethanol, 1,10-phenanthroline ( $C_{12}H_8N_2$ ), *tert*-butyl alcohol (TBA), methanol (MeOH), 1,4-benzoquinone (BQ), acetone and ascorbic acid ( $H_2A$ ) were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. All the solutions were prepared with deionized water before each run.

### 2.2. Synthesis of $H_2A/Fe^0$

The  $H_2A/Fe^0$  was synthesized in an anaerobic glove box under the protection of purified  $N_2$ . First, a 0.5 M solution of  $Fe^{2+}$  was prepared by dissolving  $FeSO_4 \cdot 7H_2O$  in deionized water (100 mL). Then, a certain volume stabilizer ( $H_2A$ , 10 g  $L^{-1}$ ) solution was added into the  $FeSO_4$  solution with electromagnetic stirring for 15 min. After intensive mixing, 100 mL of 1.5 M of  $KBH_4$  solution was added dropwise into the mixture solution. After delivering all of the  $KBH_4$  solution, the solution was stirred continuously for 30 min. Subsequently, the solid precipitation was filtered with a 0.45  $\mu m$  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  $H_2A/Fe^0$  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  $H_2SO_4$  (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  $\mu m$  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.<sup>22</sup> 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  $H_2A/Fe^0$  and  $Fe^0$  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  $H_2A/Fe^0$  and  $Fe^0$  particles were studied by Fourier transform infrared spectroscopy (FTIR, Perkin-Elmer Instrument Co. Ltd., USA). The element valence and chemical groups of  $H_2A/Fe^0$  and  $Fe^0$  were determined by X-ray photoelectron spectroscopy using monochromatic Mg K $\alpha$  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  $H_2A/Fe^0$  particles on PS activation for RhB degradation under the same operating conditions. As shown in Fig. 1a, about 35.28% RhB was removed by  $Fe^0$  alone, and only 31.33% RhB was removed by  $H_2A/Fe^0$  within 90 min, indicating that some of the reactive sites might be blocked by the excessive dispersant coated on the  $Fe^0$  surfaces. The removal efficiency for RhB was apparently improved when the reaction time was prolonged, mainly because of desorption of  $H_2A$  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.<sup>23</sup> In addition, activation of PS by  $Fe^0$  was also



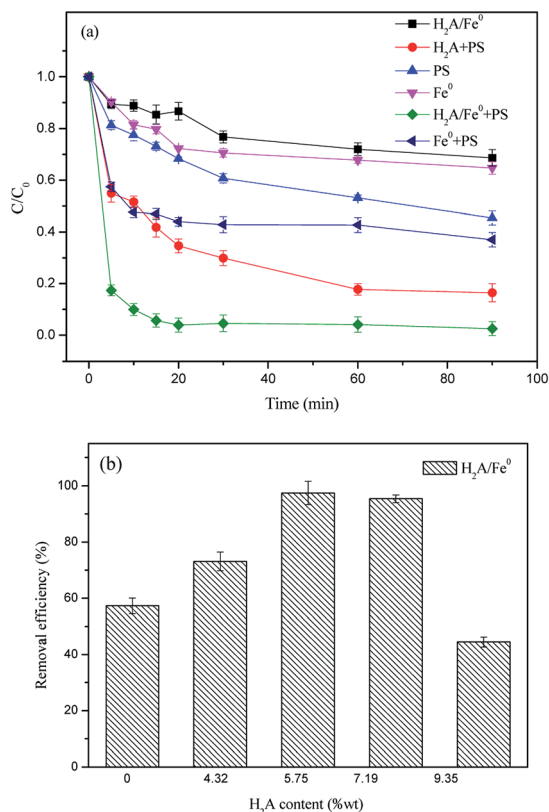
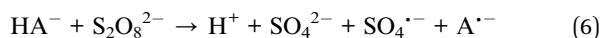
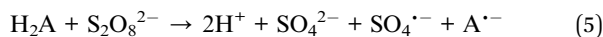


Fig. 1 (a) Comparison of removal efficiency of RhB in different systems ( $C_0 = 50 \text{ mg L}^{-1}$ , PS dosage =  $1.4 \text{ g L}^{-1}$ ,  $\text{Fe}^0$  dosage =  $1 \text{ g L}^{-1}$ ,  $\text{H}_2\text{A}/\text{Fe}^0$  dosage =  $1 \text{ g L}^{-1}$ ,  $\text{H}_2\text{A}$  dosage =  $1.6 \text{ g L}^{-1}$  and  $T = 298 \text{ K}$ ); (b) effect of  $\text{H}_2\text{A}$  concentration on removal efficiency of RhB in the  $\text{H}_2\text{A}/\text{Fe}^0$ -PS system ( $C_0 = 50 \text{ mg L}^{-1}$ ,  $\text{Fe}^0$  dosage =  $0.8 \text{ g L}^{-1}$ ,  $T = 298 \text{ K}$  and the solution volume is  $50 \text{ mL}$ ).

investigated, and the results showed that approximately 18% of the RhB was removed over 60 min in the  $\text{Fe}^0/\text{PS}$  system. A slightly improved removal efficiency of RhB was achieved in the  $\text{H}_2\text{A}/\text{PS}$  system because  $\text{H}_2\text{A}$  can react with PS to generate  $\text{SO}_4^{\cdot-}$ , according to eqn (5) and (6).<sup>24</sup> However, more than 90% of the RhB was removed with  $\text{H}_2\text{A}/\text{Fe}^0$  activated PS. Therefore, the high activity of the  $\text{H}_2\text{A}/\text{Fe}^0$  composites for PS activation was assumed to be the result of the existence of a synergistic effect in this system.



The reactivity of  $\text{H}_2\text{A}/\text{Fe}^0$  particles with different  $\text{H}_2\text{A}$  content was further investigated. As shown in Fig. 1b, the highest removal efficiency was achieved with an  $\text{H}_2\text{A}$  solution addition amount of 3.60% wt (to  $\text{Fe}^{2+}$ ) during the synthesis process of  $\text{Fe}^0$ . For an  $\text{H}_2\text{A}$  addition content higher than 3.60%, the excess  $\text{H}_2\text{A}$  might occupy the available reactive sites of  $\text{Fe}^0$  particles and then block the target pollutants diffusing onto the surface sites. In contrast, insufficient loading of the coating onto the surface of  $\text{Fe}^0$  might result in ineffective dispersion of the  $\text{Fe}^0$ ,

indicating that the optimal  $\text{H}_2\text{A}$  concentration would be 3.60%. Therefore, 3.60% was selected in the following characterization and degradation experiments.

### 3.2. Characterization of $\text{H}_2\text{A}/\text{Fe}^0$

The morphology of the  $\text{Fe}^0$  and  $\text{H}_2\text{A}/\text{Fe}^0$  was observed by TEM and FE-SEM. The TEM observation (Fig. 2a) on the  $\text{Fe}^0$  shows that bare  $\text{Fe}^0$  particles were aggregated and featured as a necklace-like chain of length 80–100 nm. When  $\text{H}_2\text{A}$  was added, the dispersion of  $\text{Fe}^0$  was significantly increased (Fig. 2b), indicating that  $\text{H}_2\text{A}$  could act as a dispersant for  $\text{Fe}^0$  nanoparticles. The particle size of  $\text{H}_2\text{A}/\text{Fe}^0$  ranges from 20 to 80 nm. The reason might be that the added  $\text{H}_2\text{A}$  could coordinate with ferrous ions to indirectly control the growth of iron particles, resulting in the smaller size of the  $\text{H}_2\text{A}/\text{Fe}$  composite.

Fig. 2c shows the representative FE-SEM image of the as-synthesized bare  $\text{Fe}^0$ , 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.<sup>21</sup> Comparatively, with the coating of  $\text{H}_2\text{A}$ , it can be observed that the  $\text{H}_2\text{A}/\text{Fe}^0$  had a smaller size than bare  $\text{Fe}^0$  (Fig. 2d). Simultaneously, the EDS spectrum further revealed the successful incorporation of  $\text{H}_2\text{A}$  and iron nanoparticles (Fig. 3e).

In order to prove the existence of functional groups of  $\text{H}_2\text{A}$  on the surface of the Fe nanoparticles,  $\text{Fe}^0$  and  $\text{H}_2\text{A}/\text{Fe}^0$  were analyzed by FTIR spectroscopy. As shown in Fig. 3, the absorption peak on  $\text{H}_2\text{A}/\text{Fe}^0$  at about  $3417 \text{ cm}^{-1}$  was significantly larger than that on  $\text{Fe}^0$ , which was attributed mainly to stretching vibrations of  $-\text{OH}$ .<sup>25</sup> In addition, compared with the

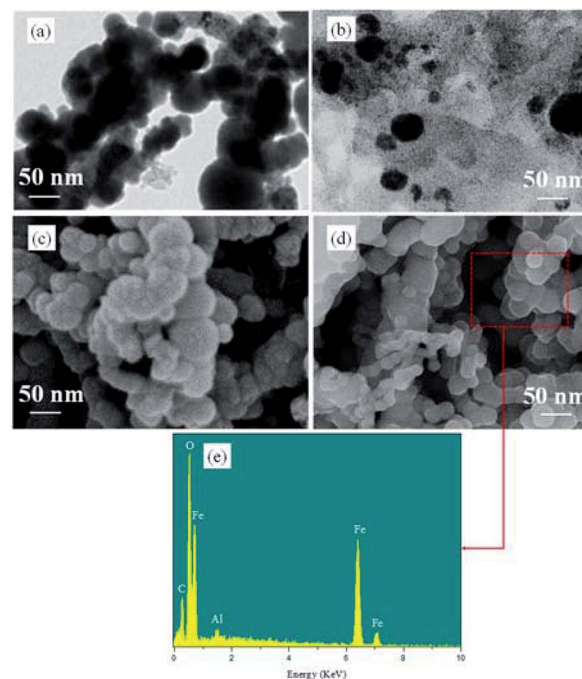


Fig. 2 TEM images of (a)  $\text{Fe}^0$  and (b)  $\text{H}_2\text{A}/\text{Fe}^0$ , FE-SEM images of (c)  $\text{Fe}^0$  and (d)  $\text{H}_2\text{A}/\text{Fe}^0$ , and (e) electron diffusion spectroscopy elemental analysis.



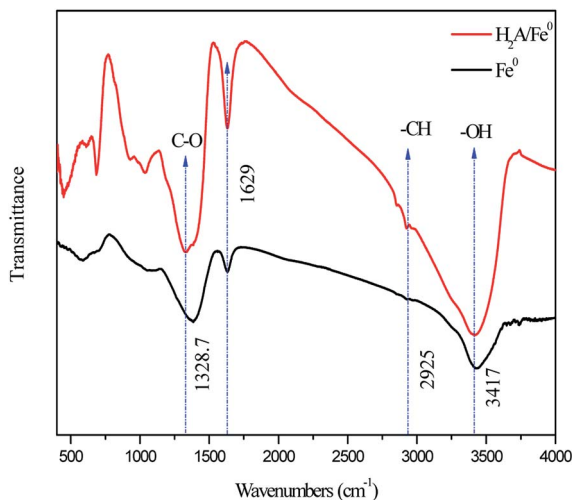


Fig. 3 FTIR spectra of  $\text{Fe}^0$  and  $\text{H}_2\text{A}/\text{Fe}^0$ .

spectrum of  $\text{Fe}^0$ , there are several inconspicuous infrared characteristic peaks for  $\text{H}_2\text{A}/\text{Fe}^0$ , among which the absorption peak appearing at approximately  $2925\text{ cm}^{-1}$  was assigned to  $-\text{CH}$ . The bands at  $1328.7\text{ cm}^{-1}$  are attributed to  $\text{C}-\text{O}$  vibrations. Meanwhile, an additional adsorption peak at  $1629\text{ cm}^{-1}$  corresponded to the stretching vibrations of  $\text{C}=\text{C}$  groups, indicating the presence of the  $\text{H}_2\text{A}$  constituent.<sup>15</sup>

XPS was used to investigate the composition and chemical state of  $\text{Fe}^0$  before and after coating by  $\text{H}_2\text{A}$ . The full-range survey spectra of  $\text{Fe}^0$  and  $\text{H}_2\text{A}/\text{Fe}^0$  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  $\text{Fe}^0$  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.<sup>26</sup> Detailed XPS patterns for the C 1s regions of the  $\text{Fe}^0$  and  $\text{H}_2\text{A}/\text{Fe}^0$  particles are presented in Fig. 4b and c. Compared with  $\text{Fe}^0$ , a conspicuous peak at  $284.7\text{ eV}$  appeared in the spectrum of  $\text{H}_2\text{A}/\text{Fe}^0$ , corresponding to  $\text{C}=\text{C}$  species, verifying the presence of  $\text{H}_2\text{A}$ . All the above characterization results of FTIR and XPS confirmed that  $\text{H}_2\text{A}$  had been successfully coated onto  $\text{Fe}^0$ .

### 3.3. Factors affecting RhB degradation in the $\text{H}_2\text{A}/\text{Fe}^0$ -PS system

The effects of PS dosage,  $\text{H}_2\text{A}/\text{Fe}^0$  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  $0.3\text{ g L}^{-1}$ . Since PS was the  $\text{SO}_4^{\cdot-}$  donor, a higher PS dosage would improve the formation of  $\text{SO}_4^{\cdot-}$ . However, when the PS dosage was further increased to  $0.5\text{ g L}^{-1}$ , it led to a decline in RhB degradation efficiency. Similar results were also reported in other studies.<sup>27</sup> A reasonable explanation for this phenomenon is that the excess  $\text{S}_2\text{O}_8^{2-}$  may lead to  $\text{SO}_4^{\cdot-}$  scavenging (eqn (7)) and the reaction between two  $\text{SO}_4^{\cdot-}$  (eqn (8)).<sup>28</sup> Hence,  $0.3\text{ g L}^{-1}$

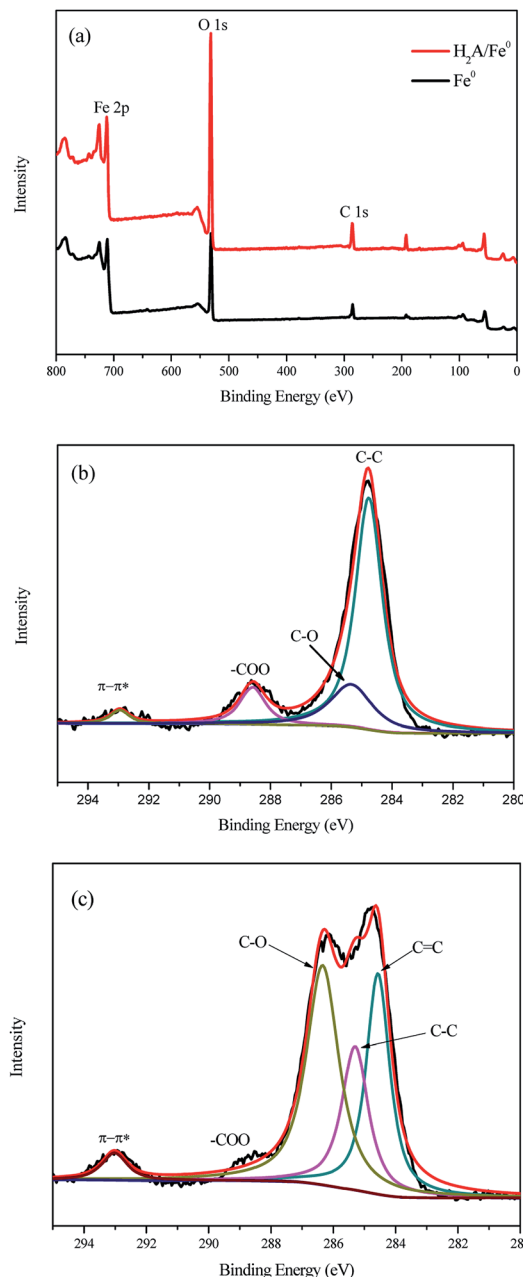
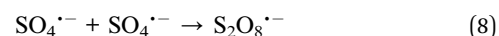
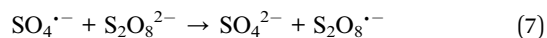


Fig. 4 XPS spectra of  $\text{Fe}^0$  and  $\text{H}_2\text{A}/\text{Fe}^0$ : (a) full-range XPS spectra, (b) C 1s regions of  $\text{Fe}^0$ , and (c) C 1s regions of  $\text{H}_2\text{A}/\text{Fe}^0$ .

PS was selected as the optimal dosage in the following experiments.



The effect of  $\text{H}_2\text{A}/\text{Fe}^0$  dosage on RhB degradation was evaluated with the  $\text{H}_2\text{A}/\text{Fe}^0$  dosage ranging from  $0.15$  to  $0.60\text{ g L}^{-1}$ . As shown in Fig. 5b, the increase in the activator dosage significantly promoted the degradation of RhB, which may be because the increase in  $\text{H}_2\text{A}/\text{Fe}^0$  dosage could provide more





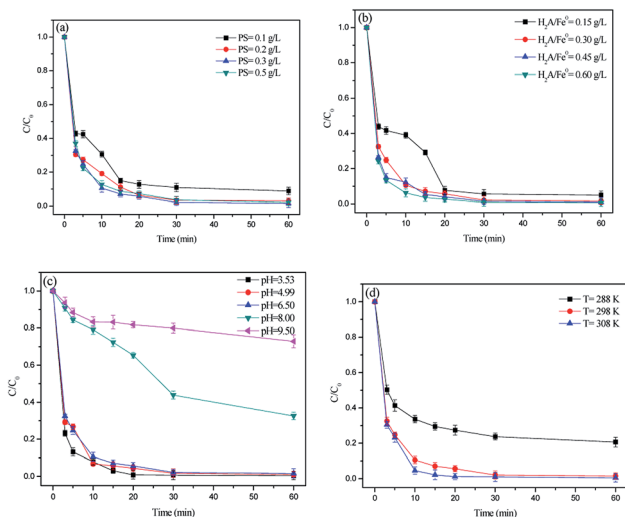
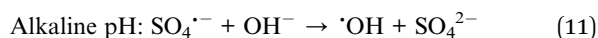
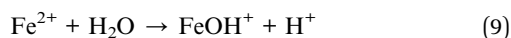


Fig. 5 Parameters affecting the degradation of RhB: (a) PS dosage, (b) H<sub>2</sub>A/Fe<sup>0</sup> dosage, (c) pH value, and (d) temperature. Except for the investigated parameter, other parameters were fixed at C<sub>0</sub> = 50 mg L<sup>-1</sup>, PS = 0.3 g L<sup>-1</sup>, H<sub>2</sub>A/Fe<sup>0</sup> = 0.3 g L<sup>-1</sup>, pH = 6.50 and T = 298 K.

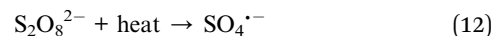
active sites for the activation of PS, thus producing more reactive free radicals for more efficient RhB degradation. At a lower dosage of H<sub>2</sub>A/Fe<sup>0</sup> (0.15 g L<sup>-1</sup>), 94.44% removal could be obtained within 30 min, indicating the excellent activity of H<sub>2</sub>A/Fe<sup>0</sup> for PS activation with 50 mg L<sup>-1</sup> RhB.

Fig. 5c shows the RhB degradation in the H<sub>2</sub>A/Fe<sup>0</sup>-PS system with different initial pH values ranging from 3.53 to 9.50. The pH value played an important parameter in the degradation of contaminants.<sup>29</sup> It could be observed that the highest RhB removal was achieved at an initial pH value of 3.53, and the removal efficiency obviously increased as the pH value decreased. This result is in accordance with Leng *et al.*'s report, which suggested that the degradation rate was lowered under neutral and alkaline conditions.<sup>30</sup> The better performance under acidic conditions in the present study may be because: (1) At lower pH values, the Fe<sup>0</sup> corrosion rate could be accelerated, leading to much faster release of Fe<sup>2+</sup>, which favors the induction of eqn (1) to produce more SO<sub>4</sub><sup>•-</sup>. (2) At a pH higher than 7, the formation of Fe<sup>2+</sup> complexes could inhibit PS activation by eqn (9). Also, the reactions between SO<sub>4</sub><sup>•-</sup> and H<sub>2</sub>O/OH<sup>-</sup> could result in the rapid decay of SO<sub>4</sub><sup>•-</sup> (eqn (10) and (11)).<sup>31</sup> 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.



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 H<sub>2</sub>A/Fe<sup>0</sup>, which could be associated with the thermal activation of PS to generate free radicals (eqn (12)),<sup>32</sup> as well as the acceleration of the reaction between H<sub>2</sub>A/Fe<sup>0</sup> and PS, probably because the diffusion and mobility of RhB molecules increased.



### 3.4. Degradation mechanism

**3.4.1 Identification of free radicals in the H<sub>2</sub>A/Fe<sup>0</sup>-PS system.** It has been reported that a series of reactive oxygen species, *e.g.*, SO<sub>4</sub><sup>•-</sup>, <sup>•</sup>OH and superoxide anion radicals (O<sub>2</sub><sup>•-</sup>), were generated in a PS/Fe(II)/hydroxylamine (HA) system and may also be generated in the H<sub>2</sub>A/Fe<sup>0</sup>-PS system.<sup>33</sup> In order to evaluate the major radical species for the RhB oxidation reaction, scavenging experiments were performed in the H<sub>2</sub>A/Fe<sup>0</sup>-PS system by adding MeOH, TBA and BQ into the reaction solution. MeOH (with α-hydrogen) is an effective quencher for both <sup>•</sup>OH (1.2 × 10<sup>9</sup> to 2.8 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>) and SO<sub>4</sub><sup>•-</sup> (1.6 × 10<sup>7</sup> to 7.7 × 10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup>). In contrast, TBA (without α-hydrogen) has an approximately 1000 times greater rate constant with <sup>•</sup>OH (3.8 × 10<sup>8</sup> to 7.6 × 10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup>) than with SO<sub>4</sub><sup>•-</sup> (4.0 × 10<sup>5</sup> to 9.1 × 10<sup>5</sup> M<sup>-1</sup> s<sup>-1</sup>).<sup>6,34</sup> Therefore, MeOH was used to scavenge both radicals, and TBA was used to selectively scavenge <sup>•</sup>OH. Moreover, we used BQ as an effective scavenger of O<sub>2</sub><sup>•-</sup> by electron transfer to generate benzoquinone radicals.<sup>35</sup>

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 O<sub>2</sub><sup>•-</sup>, SO<sub>4</sub><sup>•-</sup> and <sup>•</sup>OH are generated in the H<sub>2</sub>A/Fe<sup>0</sup>-PS system. Similar findings were reported by a previous study.<sup>36</sup> It can be preliminarily inferred that O<sub>2</sub><sup>•-</sup> may be derived from catalytic hydrolysis of PS

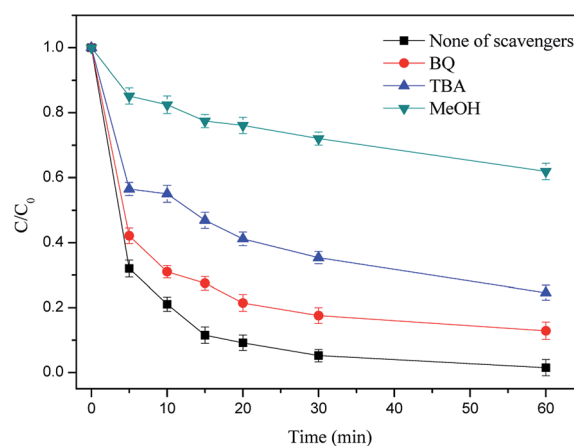
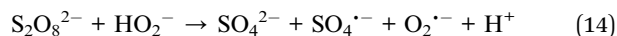
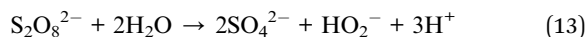


Fig. 6 Effect of different radical quenching agents on RhB removal. Reaction conditions: C<sub>0</sub> = 50 mg L<sup>-1</sup>, PS = 0.3 g L<sup>-1</sup>, H<sub>2</sub>A/Fe<sup>0</sup> = 0.3 g L<sup>-1</sup>, pH = 6.50 and T = 298 K.



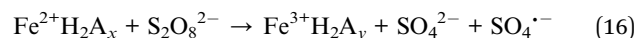
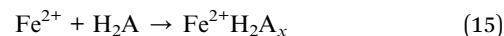
in accordance with eqn (13) and (14). Hence, the scavenging studies clearly prove the simultaneous participation of  $\text{O}_2^{\cdot-}$ ,  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  in the  $\text{H}_2\text{A}/\text{Fe}^0$ -PS oxidation process, and  $\text{SO}_4^{\cdot-}$  played a major role in achieving a good oxidation reaction.



**3.4.2 UV-vis spectral changes.** The UV-vis spectra were used to observe changes during the degradation of RhB by the  $\text{H}_2\text{A}/\text{Fe}^0$ -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 (554 nm), respectively. The UV absorbance at 259 nm corresponds to the existence of aromatic rings in RhB. The visible absorbance at 554 nm is responsible for the RhB coloration due to the conjugated structure of the C=N and C=O groups. COD removal of the RhB aqueous solution was measured to evaluate the mineralization of RhB. The COD removal efficiency of RhB reached 87.6% in 60 min, indicating that the majority of RhB was mineralized and the  $\text{H}_2\text{A}/\text{Fe}^0$ -PS system has a high capacity for degradation of RhB. This result is further confirmed by 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.<sup>37</sup> First, the decrease in the main chromophore band of RhB at 554 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.<sup>38,39</sup>

**3.4.3 The role of  $\text{H}_2\text{A}$  in enhancing RhB degradation.** The role of  $\text{H}_2\text{A}$  on enhancing RhB degradation in the  $\text{H}_2\text{A}/\text{Fe}^0$ -PS system was investigated. First of all, it is generally recognized that  $\text{H}_2\text{A}$  is a potent antioxidant agent with the ability to prevent the aggregation of  $\text{Fe}^0$  by the effect of coating (Fig. 2b and d).<sup>40</sup> In addition,  $\text{H}_2\text{A}$  is a weak acid with the ability to solubilize metal ions by  $\text{Fe}^{2+}$ - $\text{H}_2\text{A}$  ( $\text{Fe}^{2+}/\text{H}_2\text{A}_x$ ) 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  $\text{SO}_4^{\cdot-}$ , but also react with  $\text{O}_2$  to produce  $\text{O}_2^{\cdot-}$  in accordance with eqn (17).<sup>40</sup> Besides its acidity,  $\text{H}_2\text{A}$  can also serve as a reducing agent, which is capable of effectively reducing  $\text{Fe}^{3+}$  and realizing  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox cycles in the system (eqn (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  $\text{H}_2\text{A}/\text{Fe}^0$ . By contrast, the leaching of iron was faster during the oxidation of RhB by the  $\text{H}_2\text{A}/\text{Fe}^0$  composite than by pristine  $\text{Fe}^0$ , and this result further confirms the pronounced weak acid effect of  $\text{H}_2\text{A}$  with the ability to solubilize metal ions. Moreover, the ferrous iron concentration was found to increase from 22.32 to 29.11  $\text{mg L}^{-1}$  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  $\text{H}_2\text{A}$  to both the surface and dissolved  $\text{Fe}^{3+}$  *via* eqn (18), resulting in an effective  $\text{Fe}^{3+}/\text{Fe}^{2+}$  cycle. As expected, the reductive effect of  $\text{H}_2\text{A}$  was also promoted to form more and more  $\text{Fe}^{2+}$  and  $\text{SO}_4^{\cdot-}$  in the  $\text{H}_2\text{A}/\text{Fe}^0$ -PS system, which results in an acceleration in RhB degradation.

The  $\text{H}_2\text{A}/\text{Fe}^0$ -PS system exhibits significant superiority for the removal of RhB. Fig. 9 illustrates the proposed conceptual model of the RhB removal process by the  $\text{H}_2\text{A}/\text{Fe}^0$ -PS system. The superiority of the  $\text{H}_2\text{A}/\text{Fe}^0$ -PS system is mainly attributed to: (1)  $\text{H}_2\text{A}$  can reduce the structure size of  $\text{Fe}^0$  particles and increase their dispersibility; however, considering that the aggregation of  $\text{H}_2\text{A}/\text{Fe}^0$  was still remarkable (Fig. 2b and d), we

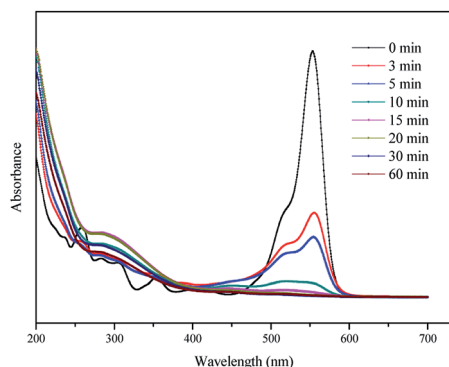


Fig. 7 UV-vis adsorption spectra of RhB at various times by the  $\text{H}_2\text{A}/\text{Fe}^0$ -PS system.

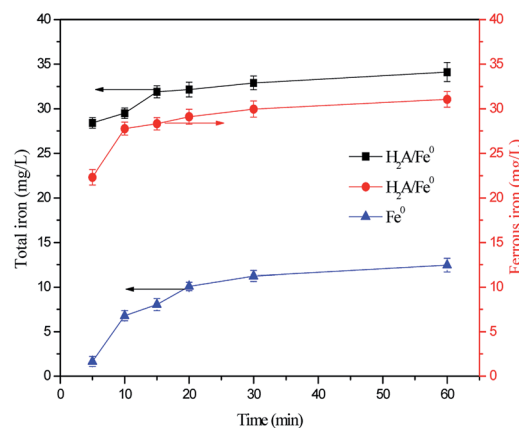


Fig. 8 Variation in total iron and ferrous iron concentrations in solution. Reaction conditions:  $C_0 = 50 \text{ mg L}^{-1}$ ,  $\text{PS} = 0.3 \text{ g L}^{-1}$ ,  $\text{H}_2\text{A}/\text{Fe}^0 = 0.3 \text{ g L}^{-1}$ ,  $\text{pH} = 6.50$  and  $T = 298 \text{ K}$ .



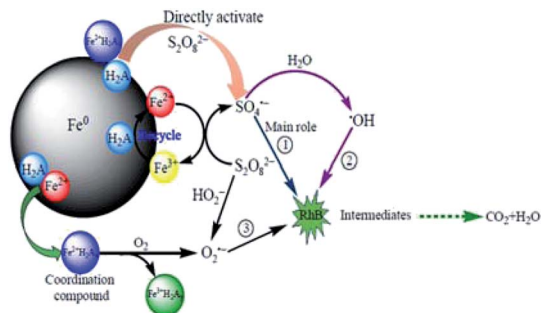


Fig. 9 Conceptual model of the RhB removal process by the  $\text{H}_2\text{A}/\text{Fe}^0$ -PS system.

believe that the high activation performance of  $\text{H}_2\text{A}/\text{Fe}^0$  was not mainly due to the increased dispersibility in solution. (2)  $\text{H}_2\text{A}$  is a weak acid that has the ability to solubilize metal ions by  $\text{Fe}^{2+}/\text{H}_2\text{A}_x$  complex formation, resulting in another pathway for the production of  $\text{O}_2^{\cdot-}$  by eqn (17), which is helpful for improving the degradation. (3)  $\text{H}_2\text{A}$  can also serve as a reducing agent, and the presence of  $\text{H}_2\text{A}$  accelerated the redox cycle of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and robust  $\text{Fe}^{2+}$  regeneration to promote RhB degradation. Therefore, this  $\text{H}_2\text{A}/\text{Fe}^0$ -PS system can produce more  $\text{SO}_4^{\cdot-}$  and  $\text{O}_2^{\cdot-}$  than the  $\text{Fe}^0$ -PS system alone. In a word, the  $\text{H}_2\text{A}/\text{Fe}^0$ -PS system involved the generation of  $\cdot\text{OH}$ ,  $\text{SO}_4^{\cdot-}$  and  $\text{O}_2^{\cdot-}$  species, among which  $\text{SO}_4^{\cdot-}$  played a key role in the degradation of RhB.

## 4. Conclusions

In this study, we present  $\text{H}_2\text{A}/\text{Fe}^0$  nanoparticles as a heterogeneous PS activator for the effective degradation of RhB. The physical-chemical properties of  $\text{H}_2\text{A}/\text{Fe}^0$  nanoparticles were characterized by TEM, FE-SEM, FTIR and XPS. Compared with bare  $\text{Fe}^0$ , the  $\text{H}_2\text{A}/\text{Fe}^0$  composites showed much higher performance for PS activation for RhB degradation. We explored the role of  $\text{H}_2\text{A}$  and concluded that both its reduction and chelating ability contribute to the good performance of the  $\text{H}_2\text{A}/\text{Fe}^0$ -PS system. In addition, the radical scavenging tests clearly confirmed the generation of  $\text{SO}_4^{\cdot-}$ ,  $\cdot\text{OH}$  and  $\text{O}_2^{\cdot-}$  and that the primary reactive oxygen species is  $\text{SO}_4^{\cdot-}$  in the  $\text{H}_2\text{A}/\text{Fe}^0$ -PS system. Batch experiments indicated that the optimal PS dosage is  $0.3 \text{ g L}^{-1}$ . RhB removal efficiency increased with increasing  $\text{H}_2\text{A}/\text{Fe}^0$  dosage and solution temperature, and it increased with a decrease in pH values. The findings in this study strongly suggested that the  $\text{H}_2\text{A}/\text{Fe}^0$  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.

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