Volume 5 | Number 9 | September 2019 | Pages 1501–1618

Environmental Science
Water Research & Technology

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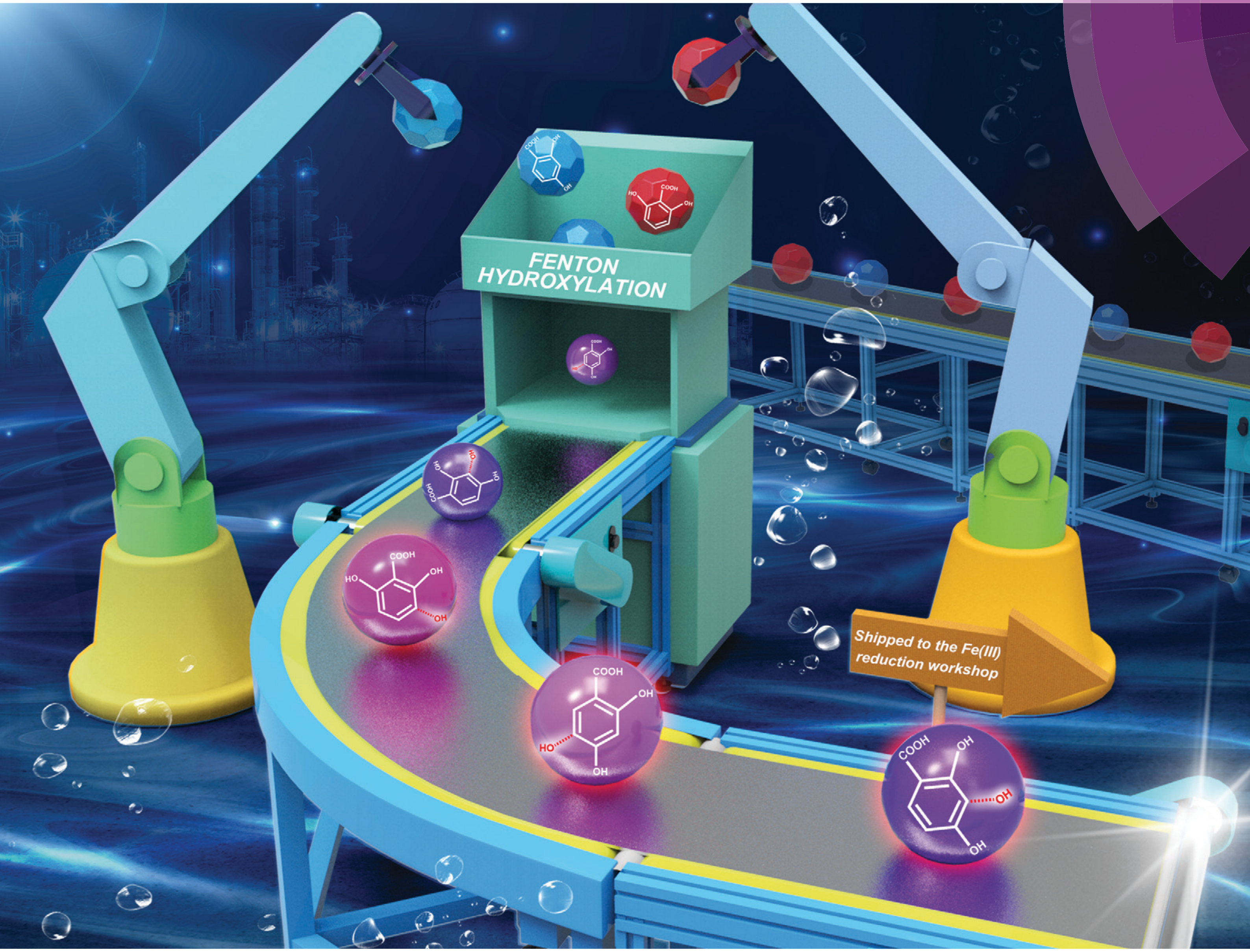

ISSN 2053-1400

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Cite this: *Environ. Sci.: Water Res. Technol.*, 2019, **5**, 1507

The reactivity and pathway of Fenton reactions driven by hydroxybenzoic acids: the effect of hydroxylation†

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Received 23rd March 2019,
Accepted 23rd July 2019

DOI: 10.1039/c9ew00250b

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Hydroxybenzoic acids (HBAs) are neglected as promoters of the Fenton reaction due to their low reduction capacity of Fe(III) and facile capture of hydroxyl radicals. However, autocatalysis often occurs in HBA degradation by the Fe(III)/H_2O_2 system. In this study, we investigated the effect of various HBA compounds on the Fenton reaction, and found that model HBAs also showed good catalytic activity. Their capability to promote the Fenton reaction is closely related to their readiness to be transformed into a hydroquinone-like (HQ-like) species. Electron-donating groups (EDGs) can accelerate the hydroxylation of aromatic compounds, thus leading to the rapid formation of a HQ-like species.

Water impact

Non-hydroquinone aromatic compounds such as hydroxybenzoic acids, which do not reduce ferric irons, are often overlooked as Fenton promoters. In this study, we found that hydroxybenzoic acids also show good co-catalytic activity, which is related to the susceptibility of these compounds to hydroxylation. This provides a new insight into developing efficient Fenton oxidation processes.

1. Introduction

Fenton oxidation processes can effectively degrade and mineralize recalcitrant pollutants by producing hydroxyl radicals ($^{\bullet}OH$, $E°(HO^{\bullet}/H_2O) = 2.8$ V/SHE).[1–3] In addition, Fenton oxidation processes have good promising applications because the Fenton reagent is environmentally friendly and low-cost.[4–6] The most widely accepted Fenton reaction mechanism was proposed by Haber and Weiss.[7]

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad k_1 = 76\ M^{-1}\ s^{-1} \qquad (1)$$

$$Fe^{3+} + H_2O_2 \rightleftharpoons Fe^{III}(HO_2)^{2+} + H^+ \rightarrow Fe^{3+} + HO_2^{\bullet} \quad k_1 = 0.001 - 0.02\ M^{-1}\ s^{-1} \qquad (2)$$

In this mechanism, the Fenton-like reaction (eqn (2)) that can regenerate ferrous ions is very slow, which limits the decomposition of H_2O_2 to produce more hydroxyl radicals.[8–12] In addition, the accumulation of ferric ions easily forms iron hydroxide sludge,[13] which causes catalyst poisoning. Many efforts have been made to optimize the efficiency of the reaction in eqn (2). For example, various iron chelators or promoters (as co-catalysts), such as thioglycolic acid, metal sulfides, and quinone–hydroquinone analogs among others are added to the Fenton system to prevent iron(III) from precipitation and accelerate the Fe^{3+}/Fe^{2+} conversion.[6,14–19]

Hydroxybenzoic acids (HBAs) are overlooked as promoters for Fenton reactions because they cannot reduce Fe(III) to Fe(II) and are prone to capturing hydroxyl radicals. Some researchers have reported that HBAs can be used to trap the $^{\bullet}OH$, such as salicylic acid,[20] 4-hydroxybenzoic acid,[21] among others.[22] Interestingly, when Fe(III) is used for the H_2O_2-mediated degradation of those HBAs, kinetic profiles displaying autocatalysis are frequently observed.[23,24] In Fenton systems, the first oxidation step is the $HO^{\bullet}$ radical addition to the aromatic ring of organic compounds to form hydroxyl cyclohexadienyl radicals that undergo different reactions to yield the primary oxidation/hydroxylation products.[25] This may lead to the generation of HQ (hydroquinone)-like species. These HQ-like species can accelerate the Fe^{3+}/Fe^{2+} conversion, which speeds up the decomposition of hydrogen peroxide to produce hydroxyl radicals. Therefore, the HBAs also have the potential to act as co-catalysts for the Fenton reactions. Unfortunately, to the best of our knowledge, little work has been done to study the reactivity and pathway of those HBAs on the Fenton degradation of pollutants.

o-Hydroxybenzoic acids (*o*-HBAs) are an important subset of HBAs. In addition, the environmental implications are also

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c9ew00250b

considered. *o*-HBAs are pollutants that are ubiquitous in many industrial waste streams. Through the autocatalytic behaviour of *o*-HBAs, it is possible to achieve a simple and efficient treatment of complex pollutants. *o*-HBAs can form complexes with ferric ions, which can effectively prevent Fe(III) from precipitation. This is good news for the Fenton reaction. In addition, the hydroxylation of benzene rings is an electrophilic substitution reaction. Electron-donating groups (EDGs) as activated groups are more conducive to the hydroxylation reaction. Therefore, salicylic acid (SA), 2,3-dihydroxybenzoic acid (2,3-DHBA), 2,4-dihydroxybenzoic acid (2,4-DHBA), 2,5-dihydroxybenzoic acid (2,5-DHBA), and 2,6-dihydroxybenzoic acid (2,6-DHBA) were chosen as the model co-catalysts for their structural features in this study (Scheme 1). To systematically study the effect of those HBAs on the Fenton degradation of pollutants, the following studies were performed in this work: (1) the formation of ferric complexes; (2) Fe(III) reduction by HBAs; (3) degradation experiments for the removal of RhB in the presence of different HBAs; (4) Fenton reaction mechanism driven by HBAs; (5) the effective pH range for the Fenton reaction driven by HBAs.

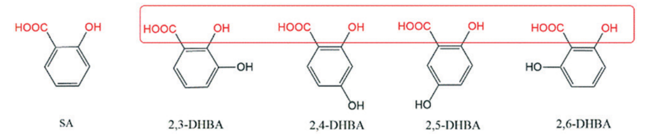
2. Materials and methods

2.1. Materials and reagents

The chemicals used were of analytical grade. Salicylic acid (SA), 2,3-dihydroxybenzoic acid (2,3-DHBA), 2,4-dihydroxybenzoic acid (2,4-DHBA), 2,5-dihydroxybenzoic acid (2,5-DHBA), 2,6-dihydroxybenzoic acid (2,6-DHBA), hydrogen peroxide (H_2O_2), and 1,10-phenanthroline monohydrate were obtained from Alfa Aesar. Rhodamine B (RhB) was acquired from Amresco. HCl, H_2SO_4, H_3PO_4, NaOH, $FeCl_3·6H_2O$, and $FeSO_4$ were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were used as received, except wherever mentioned. All experiments were performed in Milli-Q water. HCl and NaOH solutions were used to control the initial pH value of the solutions.

2.2. Reaction procedures

All experiments were carried out in a 100 mL cylindrical Pyrex vial under constant magnetic conditions, stirring at ambient temperature and pressure. All experiments were carried out under the following conditions: RhB (20 μM), HBAs (0.1 mM), $FeCl_3$ (0.04 mM), H_2O_2 (1 mM) at pH 4.0 unless otherwise specified. The reaction was initiated by adding H_2O_2 from a stock solution.



Scheme 1 Molecular structure of model HBAs.

2.3. Analysis

At given reaction-time intervals, samples were taken out and immediately analysed by UV-vis spectroscopy (UV-2550, Shimadzu). The concentration of RhB was determined by the spectrophotometric method at 554 nm. The reaction kinetics for Fe(II) concentrations were measured spectrophotometrically using the 1,10-phenanthroline monohydrate method (monitored at 510 nm). Electrospray ionization mass spectrometry (Bruker Q-TOF II) was used to analyze the intermediate products of the Fenton reactions driven by HBAs. The ESI-MS was conducted in the negative ion mode, with a spray voltage of 2.4 kV and a flow rate of 100 μL min^{-1}.

3. Results and discussion

3.1. The formation of ferric complexes

In this study, all five HBAs formed complexes with ferric ions. In SA, the –COOH and –OH groups were confirmed to be involved in the formation of the iron complex (Fig. 1E). Furthermore, two –OH groups could also form a complex with iron (Fig. 1F). To figure out the binding sites of Fe(III) and HBAs, intense ligand-transfer (LMCT) bands were detected over the pH range from 1 to 7 (except for 2,3-DHBA and catechol, with a pH range from 1 to 9) (Fig. 1). SA and catechol were used as references to verify the binding site of each DHBA. From Fig. 1, all of the HBAs showed a shift in the charge-transfer band due to a change in the type of complex present in the solution. Compared with the band shift of SA, 2,4-DHBA (Fig. 1A), 2,5-DHBA (Fig. 1B) and 2,6-DHBA (Fig. 1C) showed similar charge-transfer band shifts. The bidentate mono-complex ($[Fe(LH)]^{2+}$) appeared in the pH range from 1 to 4, and the formation of the bis-complex ($[Fe(LH)_2]^+$) was favored at pH 5–6. At approximately pH = 7, the formation of a tris-complex ($[Fe(LH)_3]$) was predominant. This suggests that the –COOH and –OH groups on the aromatic ring were involved in the formation of ferric complexes, and the result is consistent with previous reports.[26,27] In addition, the results showed that the above HBAs will not form tris-complexes with Fe(III) under basic pH conditions (data not shown). At pH > 7, no charge-transfer bands were observed, as was the case with catechol (Fig. 1F). This is consistent with previous reports.[24] The charge transfer bands of 2,3-DHBA looked like a combination of the salicylic acid bands and catechol bands (Fig. 1D). Under acidic pH conditions, the –COOH and –OH groups were involved in the formation of ferric complexes. Under basic pH conditions, two –OH groups were involved in the formation of ferric complexes to form a tris-complex. In addition, each Fe(III)–HBA complex solution was acidic, which is favorable for the Fenton reaction (2,3-DHBA, $pK_a = 2.91$; 2,4-DHBA, $pK_a = 2.6$; 2,5-DHBA, $pK_a = 2.95$; 2,6-DHBA, $pK_a = 1.22$).[28,29]

3.2. Fe(III) reduction by HBAs

Taking into account that the rate-limiting step in most Fenton systems is the production of Fe(II) from the Fe(III)

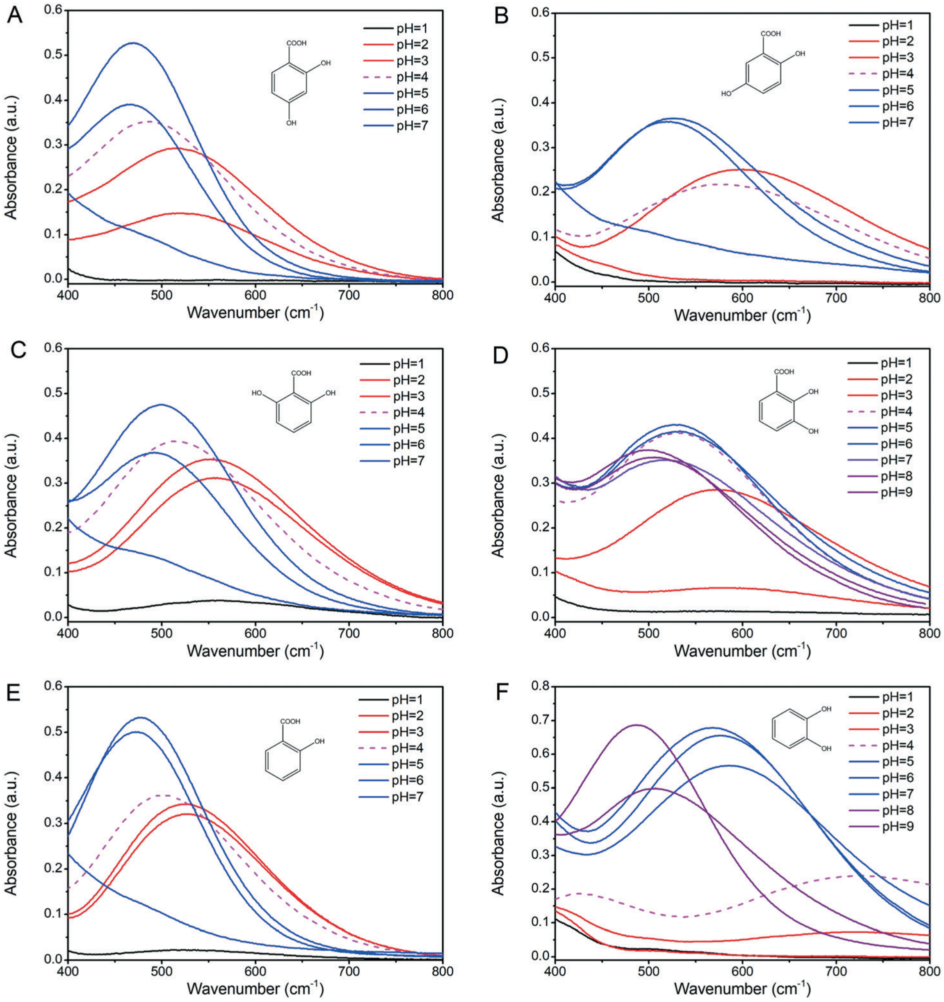


Fig. 1 UV-vis spectra of the iron complexes with (A) 2,3-DHBA, (B) 2,5-DHBA, (C) 2,6-DHBA, (D) 2,3-DHBA, (E) SA, (F) catechol. The final concentrations were 2×10^{-3} mol L^{-1} HBAs, 2×10^{-3} mol L^{-1} catechol and 2×10^{-4} mol L^{-1} FeCl$_3$. HCl and NaOH solutions were used to control the pH value of the solutions.

species, we studied the reduction of the ferric complexes. Fig. 2 shows the coupling between Fe(II) production and the absorbance of the Fe(III)–HBAs complex. It was found that 2,3-DHBA and 2,5-DHBA both promoted Fe(III) reduction (Fig. 2A and C, blue line). In addition, the absorbance of the Fe(III)–HBAs complex decreased in accordance with an increase in the Fe(II) concentration (Fig. 2A and C, red line). At 20 minutes, ferrous ions (80 μM) were generated in the Fe(III)/2,5-DHBA system (Fig. 2C), accounting for 80% of the initially added ferric ions. In the Fe(III)/2,3-DHBA system, the ferrous ion production was 45 μM (45% of the initially added ferric ions) (Fig. 2A). 2,5-DHBA has a better reducing capacity than 2,3-DHBA. In addition, 2,5-DHBA showed the best reducing activity from the initial reaction rate (Fig. 2C). However, no ferrous ions were detected in the Fe(III)/2,4-DHBA system, Fe(III)/2,6-DHBA system and Fe(III)/SA system (Fig. 2B, D and E, blue line). At the same time, there was no change in the complex absorbance (Fig. 2B, D and E, red line). This shows that 2,4-DHBA, 2,6-DHBA and SA cannot reduce the ferric ions.

Hydroquinone-like (HQ-like) or catechol-like (CAT-like) compounds can reduce ferric ions to ferrous ions and convert itself into a quinone structure. This can greatly accelerate the limiting step of the Fenton reaction (eqn (2)), thus promoting H_2O_2 to produce $^{\bullet}$OH. However, resorcinol-like (RES-like) compounds are unable to be directly oxidized by ferric ions to form a quinone structure due to the molecular structure. Table 1 shows the structures of two –OH groups in HBAs. 2,3-DHBA belongs to the CAT-like compounds and 2,5-DHBA belongs to the HQ-like compounds. Both 2,4-DHBA and 2,6-DHBA belong to the RES-like compounds. SA does not belong to any of the group. This reasonably explains the differences in the ability of the HBAs to reduce Fe(III) (Fig. 2).

3.3. Degradation experiments for the removal of RhB

In this study, Rhodamine B (RhB) was selected as the substrate to estimate the oxidizing activity of the HBA-Fenton systems. Fig. 3 shows the degradation curves of RhB *versus*

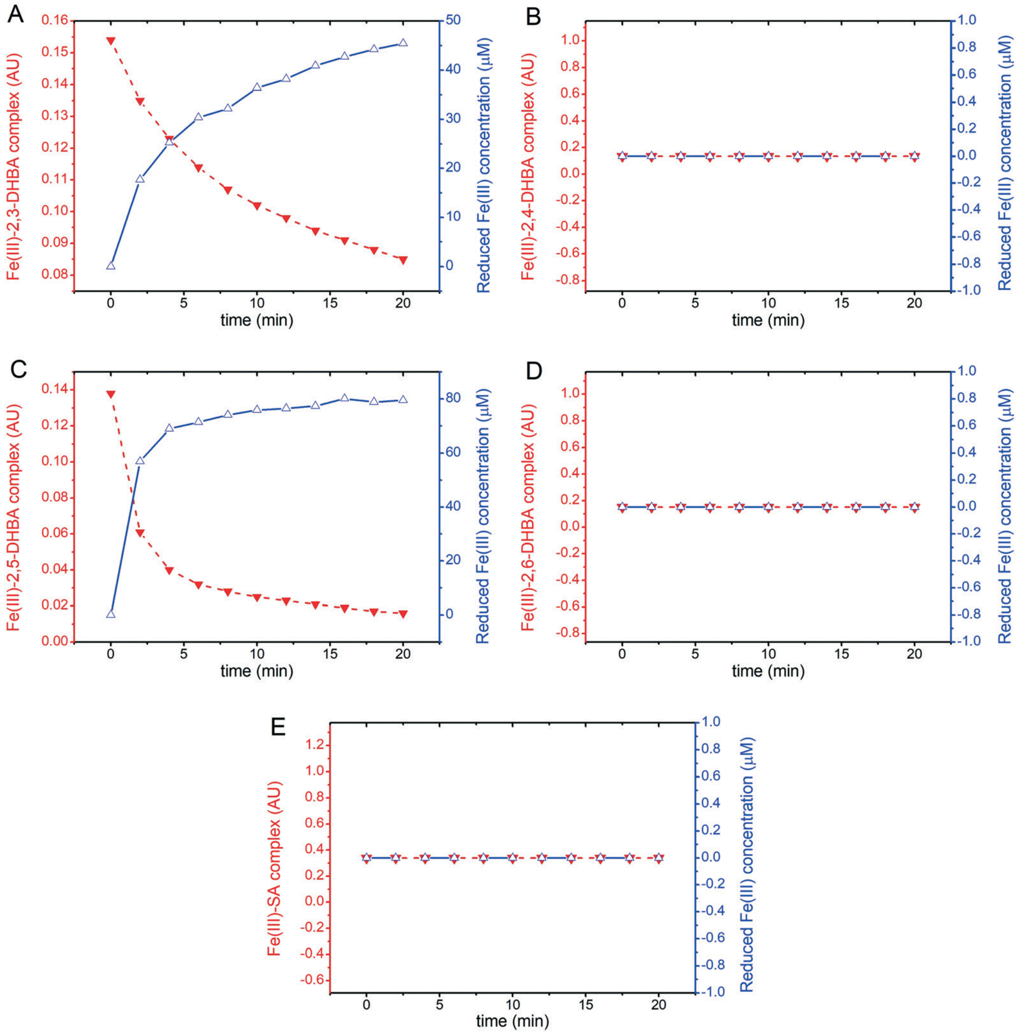
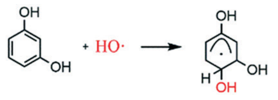
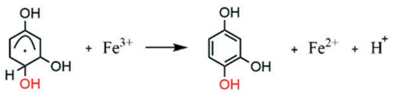


Fig. 2 Absorbance of Fe(III)–HBAs (red line) and reduced Fe(III) concentration (blue line). (A) Fe(III)/2,3-DHBA system, (B) Fe(III)/2,4-DHBA system, (C) Fe(III)/2,5-DHBA system, (D) Fe(III)/2,6-DHBA system, (E) Fe(III)/SA system. The final concentrations were HBAs (0.1 mM), $FeCl_3$ (0.1 mM), H_2O_2 (1 mM), pH = 4.0.

time under different HBA-Fenton systems. Compared with the conventional Fenton reaction (Fe(III)/H_2O_2 system), all HBAs could greatly accelerate the degradation of RhB (Fig. 3). At the beginning of the reaction, the reaction rate followed the order SA ≪ 2,4-DHBA < 2,6-DHBA < 2,3-DHBA < 2,5-DHBA. SA, 2,4-DHBA and 2,6-DHBA all presented an induction period at the beginning of the reaction (Fig. 3). This occurs because these HBAs cannot directly reduce ferric ions (Fig. 2B, D and E) and need to form HQ-like species first by hydroxylation (eqn (3)–(5)).[23]



(3)



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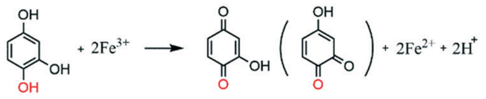

(5)

Table 1 The structures of two –OH groups in HBAs

Compound	CAT-like[a]	HQ-like	RES-like
2,3-DHBA	+	–	–
2,4-DHBA	–	–	+
2,5-DHBA	–	+	–
2,6-DHBA	–	–	+
SA	–	–	–

[a] CAT-like, HQ-like, RES-like refer to the structures bearing two –OH groups in the *ortho*, *para* and *meta* positions, respectively.

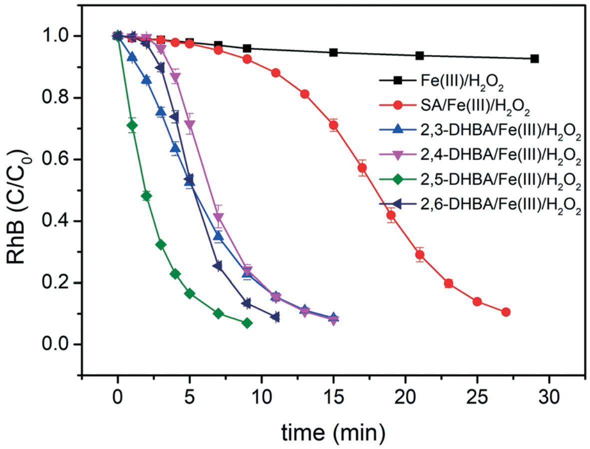

Fig. 3 Fenton degradation of RhB in the presence of different HBAs at pH 4. The final concentrations were RhB (20 μM), HBAs (0.1 mM), FeCl$_3$ (0.04 mM), H_2O_2 (1 mM).

Surprisingly, in terms of the overall reaction, the catalytic activity of the HBAs followed the order SA < 2,4-DHBA = 2,3-DHBA < 2,6-DHBA < 2,5-DHBA. 2,4-DHBA and 2,6-DHBA, with RES-like structures, have also shown excellent catalytic activities. The results showed that the catalytic activities of 2,4-DHBA and 2,6-DHBA do not depend mainly on their reduction capacity of iron, but instead depend on the formation rate of the HQ-like species. The electron-donating groups (EDGs) such as the –OH groups can activate the benzene ring, which is conducive to an electrophilic addition. The increase in the number of hydroxyl groups is more beneficial to the hydroxylation of aromatic compounds, which form HQ-like species.

3.4. The Fenton reaction mechanism driven by HBAs

Fig. 4 shows the intermediate products of HBAs in the Fenton reaction by ESI-MS. According to the ESI-MS data, we found that peaks at *m*/*z* 125.02 (trihydroxy benzene) and *m*/*z* 169.02 (trihydroxybenzoic acid) appeared in all DHBAs-Fenton systems (Fig. 4A–D). Both trihydroxy benzene and trihydroxybenzoic acid have a HQ or CAT structure and can react with ferric ions to produce ferrous ions. In addition, the peak at *m*/*z* 151.00 (carboxyl substituted quinone) was only found in the 2,3-DHBA/Fe(III)/H_2O_2 and 2,5-DHBA/Fe(III)/H_2O_2

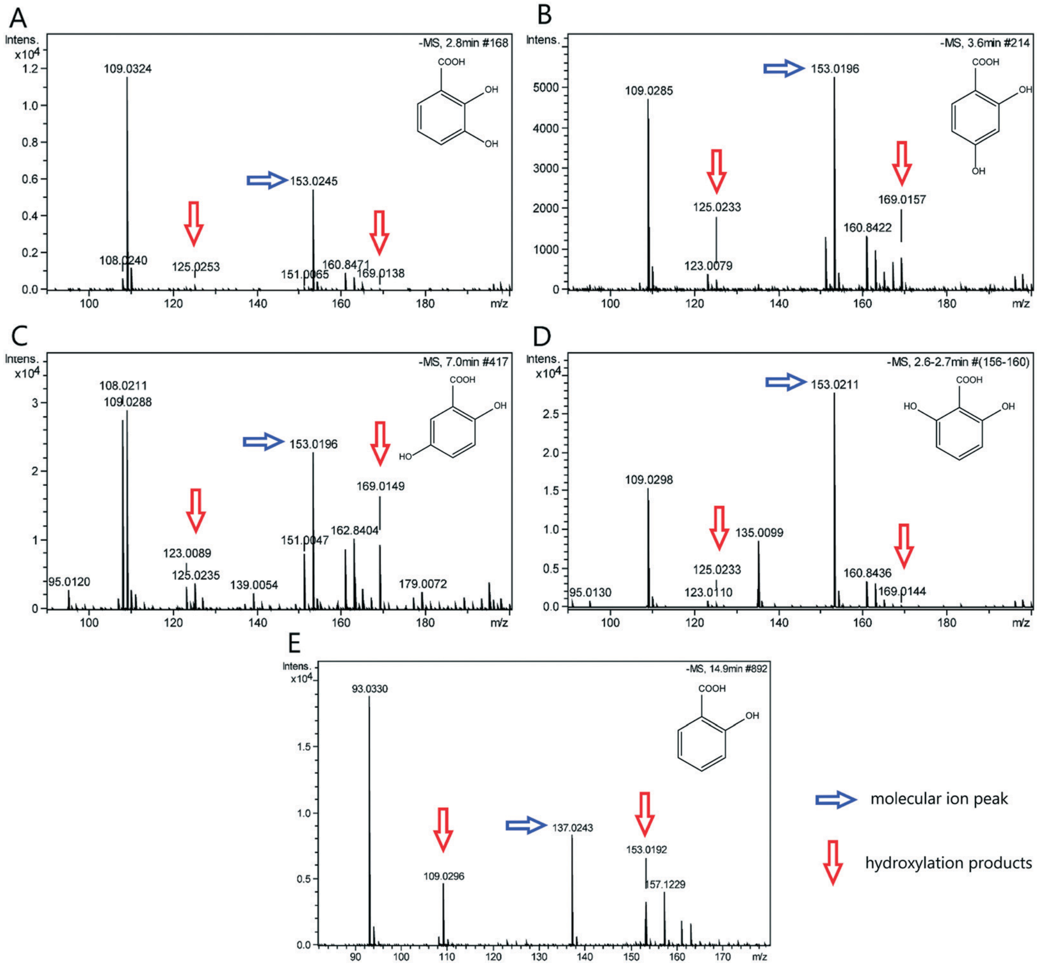

Fig. 4 The ESI-MS of the HBAs intermediate products in the different systems (HBAs: (A) 2,3-DHBA, (B) 2,4-DHBA, (C) 2,5-DHBA, (D) 2,6-DHBA, (E) SA). The final concentrations were HBAs (4 mM), FeCl$_3$ (1 mM), and H_2O_2 (10 mM). The molecular ion peak: *m*/*z* 137 SA, *m*/*z* 153 DHBAs.

systems (Fig. 4A and C). This indicates that 2,3-DHBA and 2,5-DHBA reacted with the ferric ions and then transformed themselves into quinone structures. This is consistent with the Fe(III) reduction in Fig. 2A and C. Although 2,3-DHBA and 2,5-DHBA can reduce ferric ions, we found that they also formed trihydroxybenzene and trihydroxybenzoic acid from the ESI-MS data. This indicates that all DHBAs could easily capture HO$^•$ to form the substituted hydroquinone. As electron-donating groups (EDGs), the –OH groups can increase the activity of the benzene ring and facilitate the addition of HO$^•$, and this is positively correlated with the number of –OH groups. In Fig. 4E, peaks at *m*/*z* 153.02 (DHBA) and *m*/*z* 109.02 (catechol) were found in the SA-Fenton system. This is consistent with previous reports.[30,31] According to the mass spectrometry data, this further verified that the ability of the HBAs to reduce ferric ions comes from the formation of HQ-like species.

Hydroxylation is an electrophilic substitution reaction; the addition of HO$^•$ radicals to aromatic rings bearing electron-donating groups (EDGs) (such as –OH) is mainly directed to the *ortho* and *para* positions.[32] However, the addition of the HO$^•$ radicals to aromatic rings bearing electron-withdrawing groups (EWGs) (such as $-NO_2$ and –COOH) is mainly statistical in nature.[32,33] Moreover, when both EWGs and EDGs exist, the EDGs' effect is mainly considered.[32] In addition, although the carboxyl group belongs to the EWGs, it is much more labile and a HO$^•$ attack on the benzoic acid derivatives may yield decarboxylated products.[30] So, we speculated on the possible intermediate products (Scheme S1, see ESI†) in the HBAs-Fenton system according to the hydroxyl addition rules.

In section 3.3, we found that the catalytic capacity of HBAs is not consistent with the capacity of reducing ferric ions by HBAs themselves. The quick formation of the HQ-like species

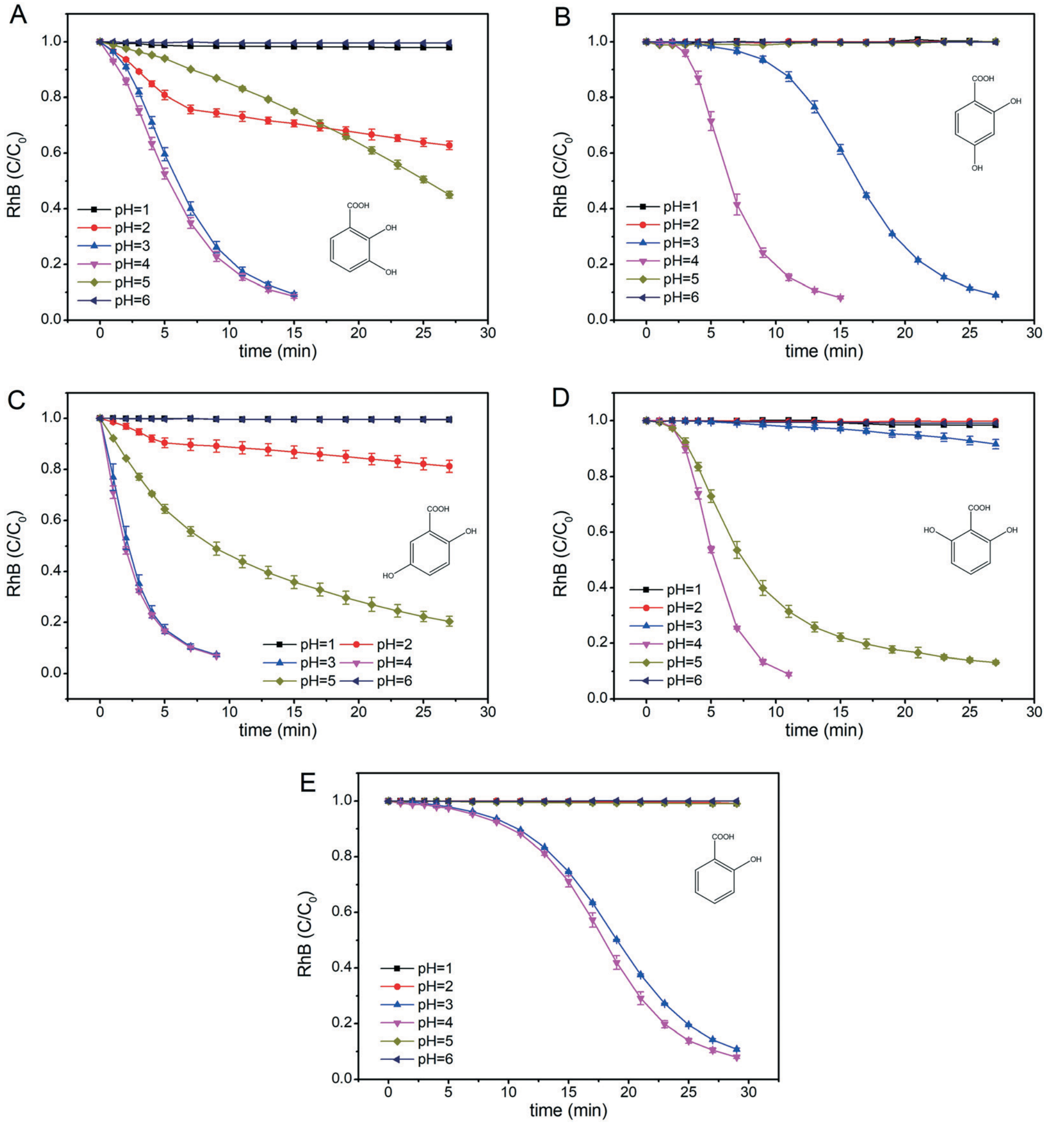

Fig. 5 Effect of pH on the Fenton degradation of RhB driven by different HBAs (HBAs: (A) 2,3-DHBA, (B) 2,4-DHBA, (C) 2,5-DHBA, (D) 2,6-DHBA, (E) SA). The final concentrations were RhB (20 μM), HBAs (0.1 mM), $FeCl_3$ (0.04 mM), H_2O_2 (1 mM).

may play an important role. To verify the effect of these hydroxylation intermediates in Fig. 4, the reduced Fe(III) concentration change of HBAs in the Fenton system were performed (Fig. S1†). From Fig. S1,† large amounts of ferrous ions were also quickly produced in the 2,4-DHBA/Fe(III)/H_2O_2 and 2,6-DHBA/Fe(III)/H_2O_2 systems in comparison with the SA/Fe(III)/H_2O_2 system. This further verifies the activation effect of EDGs on the benzene ring. This facilitates the addition of hydroxyl radicals to form the HQ-like species. In addition, the order of ferrous production catalyzed by the DHBAs is consistent with that of the RhB degradation catalyzed by the DHBAs (Fig. 3). This is consistent with the Fenton reaction mechanism being restricted by the formation rate of ferrous ions (eqn (2)).

3.5. The effect of pH on the RhB degradation

In order to avoid $Fe(OH)_3$ formation, the Fenton system is limited to acidic pH conditions. In general, the Fenton reactions have an optimal pH range (pH = 2.8–3.2).[2] A pH value that is too high or too low will affect the oxidation efficiency.[11] In this study, we further investigated the effects of pH on the degradation of RhB by the HBA-Fenton systems (Fig. 5). The optimal pH value of all Fenton reactions driven by different DHBAs was pH = 4.0. At low pH (pH = 3.0), 2,5-DHBA showed good catalytic reactivity (Fig. 2E). In addition, 2,6-DHBA showed the best catalytic activity at $pH > 4.0$. At a pH value of 5.0, the degradation percentage of RhB was 87% by 2,6-DHBA (80% by 2,5-DHBA, 55% by 2,3-DHBA) (Fig. 5D). In addition, with respect to the LMCT bands in Fig. 1, it appears that a monocomplex of HBA is more beneficial for the Fenton reaction.

4. Conclusions

In this study, we explored the activity and pathway of Fenton reactions driven by various hydroxybenzoic acids (HBAs). We found that the dihydroxybenzoic acids (DHBAs) showed excellent catalytic capacity compared with that of SA. More importantly, the catalytic activity of DHBA does not depend on its own ability to reduce ferric ions, but mainly depends on the rate of hydroxylation. The hydroxylation efficiency of the aromatic compounds mainly depends on the activation effect of the electron-donating groups. This indicates that the non-hydroquinone aromatic compounds can also effectively accelerate the Fenton reaction through hydroxylation. This provides a new way to develop an efficient Fenton oxidation process.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The work was supported by the Natural Science Foundation of China (Grants 41573115 and 21377126) and Science and Education Integration Foundation (Institute of Chemistry, Chinese Academy of Sciences, China).

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