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Hydroxylamine-facilitated removal of organic pollutants by the Fenton process

Wenyan Zhang, Longqian Wang, Xiaoyu Li, Yan Xue, Yixuan Zhao, Hao Qian, Zhuoyu Bu, Yuwei Pan*

College of Biology and the Environment, Nanjing Forestry University, Nanjing 210037, China, emails: panyw@njfu.edu.cn (Y.W. Pan), 627389011@qq.com (W.Y. Zhang), 791813206@qq.com (L.Q. Wang), 1137701827@qq.com (X.Y. Li), 2946330048@qq.com (Y. Xue), 1031135872@qq.com (Y.X. Zhao), 472456582@qq.com (H. Qian), 18339183616@163.com (Z.Y. Bu)

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ABSTRACT

The traditional Fenton process cannot efficiently remove organic pollutants because of the low recycling efficiency of Fe^{2+}. Hydroxylamine (HA) is a typical reducing agent that can accelerate the Fe^{2+} cycle. Thus, the HA-facilitated Fe^{2+}/H_2O_2 removal of tartrazine was investigated. Only 31.4% tartrazine could be removed within 10 min with the Fe^{2+}/H_2O_2 system, while 76.9% tartrazine could be removed with the Fe^{2+}-HA/H_2O_2 system. The value of k for removing tartrazine with the Fe^{2+}-HA/H_2O_2 system was 4.3-fold higher than that for removing tartrazine with the Fe^{2+}/H_2O_2 system; the effect of various factors, such HA dosage (0–8 mM), initial pH (3–6), Fe^{2+} dosage (0–0.4 mM) and H_2O_2 dosage (1–16 mM), on the tartrazine removal with the Fe^{2+}-HA/H_2O_2 system were also examined. The optimal HA, Fe^{2+}, and H_2O_2 dosages were 4, 0.2 and 8 mM, respectively. The Fe^{2+}-HA/H_2O_2 process could also broaden the working pH range from 3–4 to 3–6 for wastewater treatment. In addition, the tartrazine removal performance of the Fe^{2+}-HA/H_2O_2 process was better in the presence of inorganic ions and natural organic matter. Moreover, the Fe^{2+}-HA/H_2O_2 process could remove a wide range of organic pollutants efficiently and significantly improved of the performance of the Fe^{2+}/H_2O_2 process. Therefore, this study could improve our understanding of the effect of HA on promoting pollutant elimination with the Fe^{2+}/H_2O_2 process.

Keywords: Hydroxylamine; Tartrazine; Fe^{2+}/H_2O_2 process; Removal

1. Introduction

Currently, synthetic azo dye wastewater has attracted serious attention due to its potential toxicity to the environment and humans [1]. Among azo dyes, tartrazine is commonly used as a food coloring agent and is recalcitrant to biodegradation [2]. Advanced oxidation processes (AOPs) have generally been considered a powerful method for the treatment of nonbiodegradable and recalcitrant pollutants [3–7]. Among the AOPs, the Fenton process (Fe^{2+}/H_2O_2) is an efficient and attractive process due to its simple operation, fast reaction rate, and environmental friendliness [8]. Hydroxyl radicals ($^{\bullet}OH$) can be generated by the reaction between Fe^{2+} and H_2O_2 (Eq. (1)) [9,10]. However, Fe^{2+} could not be recycled efficiently, leading to a low efficiency for pollutant removal because the reaction between Fe^{3+} and H_2O_2 (Eq. (2)) is much slower than that between Fe^{2+} and H_2O_2 (Eq. (1)) [11]. The poor recycling of Fe^{2+} also causes an accumulation of sludge and results in the requirements of a narrow working pH range (2.5–4) and high H_2O_2 dosage [11].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \qquad k = 76\ M\ s^{-1} \tag{1}$$

* Corresponding author.

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^{\bullet} \qquad k = 0.02\ M\ s^{-1} \tag{2}$$

Currently, researchers have developed several methods to improve the performance of the Fenton process. (1) External energy was used to enhance Fenton performance, such as electro-Fenton [2], photo-Fenton [12] and sono-Fenton [13]. Although these processes could improve the pollutant removal efficiency, the input extra energy would need a complex device, which would largely increase the cost. (2) Fe^{2+} was substituted by heterogeneous catalysts, such as goethite (α-FeOOH) [14], zero-valent iron (ZVI, Fe^0) [1], hematite (α-Fe_2O_3) [15], α-Fe_2O_3/TiO_2 [16], Fe^0/Fe_3O_4 [17], Si–Al/α-FeOOH [18], and magnetite (Fe_3O_4) [19]. Heterogeneous catalysts could broaden the pH range, increase the recycling of Fe^{2+} and reduce the accumulation of sludge. However, the pollutant removal rate by heterogeneous catalyst-based Fenton processes was usually lower than that of homogeneous iron-based Fenton processes. (3) Chelating agents, such as ethylenediaminetetraacetic acid (EDTA) [20], ethylenediamine-N,N′-disuccinic acid [21], and nitrilotriacetic acid (NTA) [22], were used to chelate with Fe ions, thus preventing precipitation and promoting the performance of the Fenton process. These chelating agents also compete with $^{\bullet}OH$, for the target pollutants, thus inhibiting the pollutant removal efficiency.

Hydroxylamine (NH_2OH, HA) is a typical reducing agent that accelerates the redox cycle of Fe^{3+}/Fe^{2+} (Eq. (3) and enhances the catalysis of H_2O_2 and the production of $^{\bullet}OH$ [23]. The addition of HA could also prevent the precipitation of Fe^{3+}, thus reducing the ferric oxide sludge and expanding the working pH range [24,25]. According to previous investigations, the addition of HA could also decrease the inhibition of inorganic ions affecting the Fenton process [25]. HA has been used to enhance the performance of the $Fe@Fe_2O_3/H_2O_2$ system [11], magnetically activated carbon/γ-Fe_2O_3/H_2O_2 system [23], and $CuFeO_2/H_2O_2$ system [26] for the removal of various pollutants.

$$Fe^{3+} + NH_2OH \rightarrow NH_2O^{\bullet} + Fe^{2+} + H^+ \tag{3}$$

Therefore, the objectives of the present study were as follows: (1) investigate the performance of HA in terms of enhancing efficiency of the Fe^{2+}/H_2O_2 system for tartrazine removal; (2) investigate the affecting factors, such as HA dosage, initial pH, Fe^{2+} dosage and H_2O_2 dosage, on tartrazine removal with the Fe^{2+}-HA/H_2O_2 system; (3) investigate the effect of inorganic ions and natural organic matter (NOM) on tartrazine removal with the Fe^{2+}-HA/H_2O_2 system; and (4) investigate the performance of the Fe^{2+}-HA/H_2O_2 system for the removal of various pollutants.

2. Material and methods

2.1. Chemicals

Hydroxylamine, $FeSO_4{\cdot}7H_2O$, H_2O_2 (30%), oxalate, methanol (HPLC-grade), and phenanthroline were purchased from the Aladdin China Company. Tartrazine, rhodamine b (RhB) and orange (OG) were purchased from Meryer Chemical Technology Co., Ltd., (China). NaCl, Na_2SO_4 and $NaHCO_3$ were purchased from Nanjing Chemical Reagent Co., Ltd., (China).

2.2. Tartrazine removal experiments

Batch experiments were conducted with a volume of 250 mL in 300 mL triangular flasks at a constant stirring rate of 600 rpm. HA, $FeSO_4$, tartrazine and H_2O_2 were added to the working solution. The initial pH value of the solution was adjusted with NaOH (0.1 mol L^{-1}) and H_2SO_4 (0.1 mol L^{-1}). Samples were drawn at predetermined times, and methanol was added for the measurement.

2.3. Analytical methods

The concentrations of tartrazine, RhB, and OG were determined by UV-visible spectrophotometry (Shanghai Mapada Company, P1) at 428, 554, and 486 nm, respectively. The H_2O_2 concentration was detected by the potassium titanium oxalate method at 400 nm. Fe^{2+} ion concentrations were determined with the 1,10-phenanthroline method at 510 nm.

The pollutant removal (η/%) was calculated according to Eq. (4), and the removal rate pollutant (k) was fitted by a pseudo-first-order rate equation (Eq. (5)).

$$\eta = \frac{C_0 - C_t}{C_0} \times 100 \tag{4}$$

$$\ln \frac{C_t}{C_0} = -kt \tag{5}$$

where k is the degradation rate, C_0 (mg L^{-1}) and C_t (mg L^{-1}) are the concentration of the pollutant at time 0 and reaction time (t), respectively.

$$f = \frac{k_1}{k_2} \tag{6}$$

where k_1 and k_2 are the pseudo-first-order constants for removing pollutants with the Fe^{2+}-HA/H_2O_2 and Fe^{2+}/H_2O_2 systems, respectively.

3. Results and discussion

3.1. Tartrazine removal with various systems

As shown in Fig. 1a, the tartrazine removal with the H_2O_2, HA/H_2O_2, Fe^{2+}/H_2O_2 and Fe^{2+}-HA/H_2O_2 systems were compared. Only 2.8% tartrazine could be removed by H_2O_2 oxidation alone, demonstrating that H_2O_2 alone could not efficiently remove tartrazine. Fe^{2+} could catalyze H_2O_2 and then produce $^{\bullet}OH$; thus, 52.1% tartrazine could be removed within 60 min with the Fe^{2+}/H_2O_2 system. HA could also catalyze H_2O_2, and 38.3% tartrazine could be removed within 60 min with the HA/H_2O_2 system. HA could also accelerate the redox cycle of Fe^{3+}/Fe^{2+}, thus improving the efficiency of Fe^{2+}/H_2O_2 system, and 76.9% tartrazine could be removed within only 10 min with the Fe^{2+}-HA/H_2O_2 system. Moreover, as shown in Fig. 2b, the tartrazine removal rate with the Fe^{2+}-HA/H_2O_2 system (0.247 min^{-1}) was much higher than that with the Fe^{2+}/H_2O_2 system (0.047 min^{-1}).

The Fe^{2+} ion concentration played a critical role in pollutant removal with the Fenton system. Thus, the

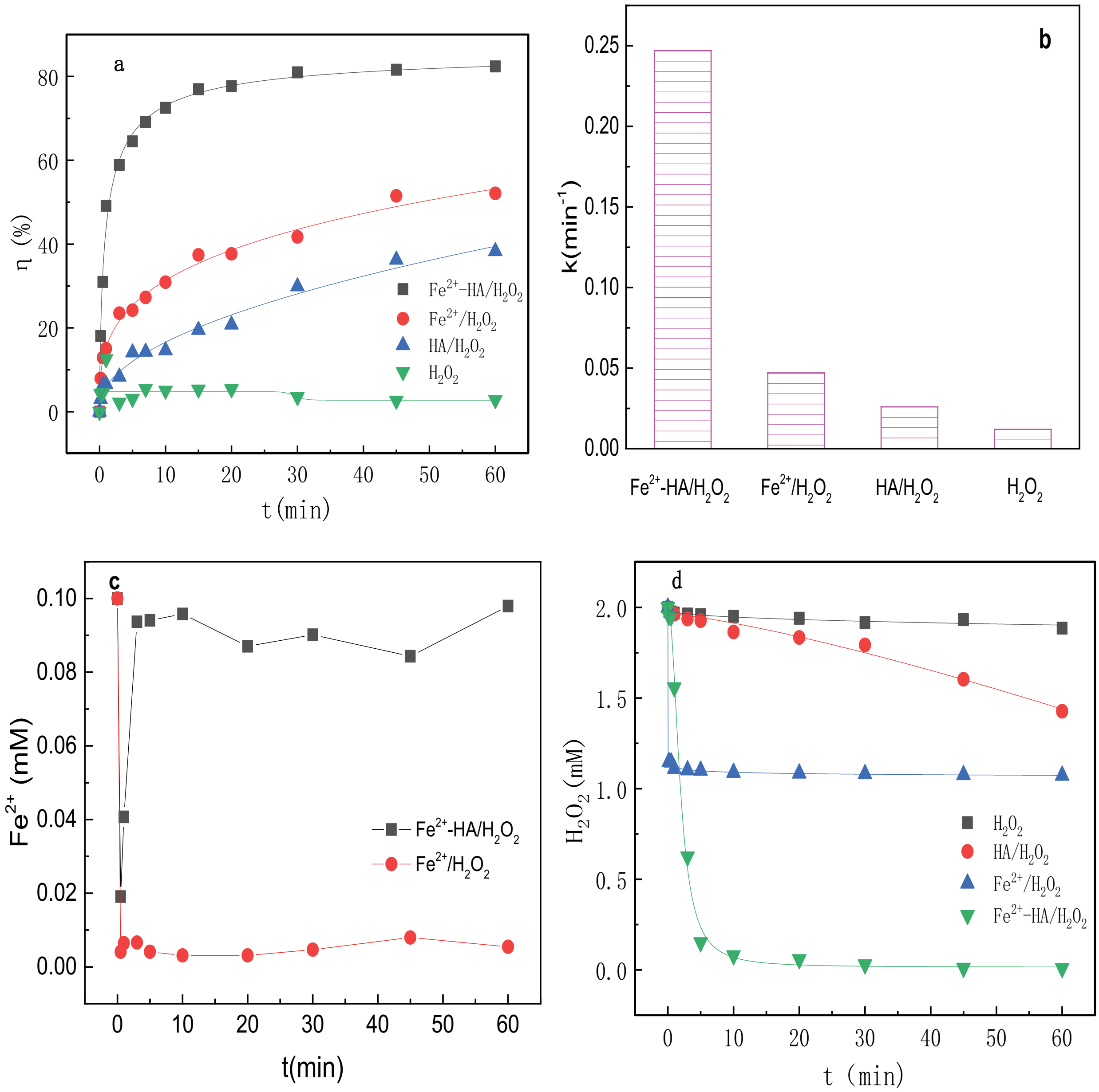

Fig. 1. (a) Tartrazine removal, (b) value of *k* for tartrazine removal, (c) Fe^{2+} concentration, and (d) H_2O_2 concentration in different systems. Reaction conditions: [Fe^{2+}] 0.1 mM; [H_2O_2] 2 mM; pH 4; [HA] 2 mM; [tartrazine] 200 mg L^{-1}.

concentration of Fe^{2+} ions was determined in both the Fe^{2+}/H_2O_2 and Fe^{2+}-HA/H_2O_2 systems. As depicted in Fig. 1c, the concentration of Fe^{2+} ions in the Fe^{2+}-HA/H_2O_2 system was much higher than that in the Fe^{2+}/H_2O_2 system. After 1 min of reaction, the concentration of Fe^{2+} ions was 0.084 mM in the Fe^{2+}-HA/H_2O_2 system, but it was only 0.008 mM in the Fe^{2+}/H_2O_2 system. A higher Fe^{2+} concentration could accelerate the catalysis of H_2O_2. As shown in Fig. 1d, the rate of the H_2O_2 catalysis in the Fe^{2+}-HA/H_2O_2 system was much faster than that in the other systems. Therefore, HA could accelerate the redox cycle of Fe^{3+}/Fe^{2+}, thereby increasing the Fe^{2+} concentration, inducing a faster H_2O_2 catalysis rate and accelerating $^{\bullet}OH$ generation for tartrazine removal.

3.2. Factors affecting tartrazine removal

3.2.1. HA concentration

HA could accelerate the redox cycle of Fe^{3+}/Fe^{2+}, thus increasing the Fe^{2+} concentration, inducing faster H_2O_2 catalysis and enhancing the generation of $^{\bullet}OH$, ultimately leading to higher tartrazine removal. Thus, HA concentrations (0–8 mM) and their effect on the tartrazine removal with the Fe^{2+}-HA/H_2O_2 system were determined. As shown in Fig. 2a, only 52.1% tartrazine could be removed within 60 min without the addition of HA. Tartrazine removal increased with increasing HA concentration. The tartrazine removal was 64.56%, 72.5%,77.5% and 79.8% within 10 min with HA added at 1, 2, 4 and 8 mM, respectively. Moreover, the value of k increased with increasing HA concentration and then nearly leveled off when the HA concentration further increased from 4 to 8 mM which might because excessive could not further accelerate the cycle of Fe^{3+}/Fe^{2+}. Therefore, the optimal HA dosage was 4 mM.

3.2.2. Initial pH

The initial pH (3–6) significantly affected the performance of the Fenton system, affecting both the Fe^{2+}/H_2O_2 and Fe^{2+}-HA/H_2O_2 systems in terms of the tartrazine removal. As shown in Figs. 3a and c, the tartrazine removal decreased significantly with increasing initial pH. The tartrazine removal decreased from 88.2% to 52.1%, 47.8% and 12.8% within 60 min, and the corresponding value of k decreased from 0.083 to 0.047, 0.039 and 0.011 min^{-1} when the initial pH increased from 3 to 4, 5, and 6, respectively. As shown in Fig. 3b, the tartrazine removal was affected slightly by the increasing pH in the Fe^{2+}-HA/H_2O_2 system. The tartrazine removal was 84.9%, 82.4%, 79.6% and 74.1% within 60 min with corresponding k values of 0.241, 0.247, 0.243 and 0.118 at initial pH values of 3, 4, 5, and 6. Although the removal rate for removing tartrazine decreased at pH 6 in the Fe^{2+}-HA/H_2O_2 system, 74.1% tartrazine could still be removed within 60 min. The performance of tartrazine removal significantly decreased with the increase of the initial pH which was attributed to the precipitation of Fe ions. While, HA could prevent the precipitation of Fe^{3+}, thus kept the good performance for tartrazine removal at nearly neutral pH in Fe^{2+}-HA/H_2O_2 system. Meanwhile, as illustrated in Fig. 3d, the pseudo-first-order constant of the tartrazine removal by the Fe^{2+}-HA/H_2O_2 process was 2.9-, 5.3-, 6.2-, and 10.6-fold higher than that of the tartrazine removal by the Fe^{2+}/H_2O_2 process at initial pH values of 3, 4, 5, and 6, respectively. Therefore, the Fe^{2+}-HA/H_2O_2 process could broaden the working pH range from 3–4 to 3–6 for wastewater treatment.

3.2.3. Fe^{2+} dosage

The Fe^{2+} concentration determines the rate of removing pollutants with the Fenton system; thus, the tartrazine removal was conducted with the Fe^{2+}-HA/H_2O_2 system at different Fe^{2+} concentrations (0–0.4 mM). As depicted in Fig. 4a, HA could catalyze H_2O_2 to remove tartrazine, and 38.3% tartrazine could be removed within 60 min without Fe^{2+} addition. The tartrazine removal increased quickly with Fe^{2+} addition and was 71.9%, 82.8%, 82.4%, 79.1% and 79.4% at 0.025, 0.05, 0.1, 0.2 and 0.4 mM, respectively. Moreover, as shown in Fig. 4b, the value of k increased from 0.021 to 0.032, 0.107, 0.235, 0.247, 0.303 and 0.367 min^{-1} when the Fe^{2+} concentration increased from 0 to 0.025, 0.05, 0.1, 0.2 and 0.4 mM. Higher Fe^{2+} concentration could catalyze H_2O_2 faster thus improved the tartrazine removal rate and the performance did not change significantly from 0.2 to 0.4 mM due to the quenching effects of Fe^{2+} according to Eq. (7) [27]. Therefore, the optimal Fe^{2+} dosage for removing tartrazine with the Fe^{2+}-HA/H_2O_2 system was 0.2 mM.

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^- \quad (7)$$

3.2.4. H_2O_2 dosage

The H_2O_2 concentration is a significant factor in the Fenton system because it is directly related to the concentration of ${}^{\bullet}OH$, and therefore, the effect of the initial H_2O_2 concentration (1–16 mM) on the tartrazine removal was investigated. As illustrated in Fig. 5a, the tartrazine removal

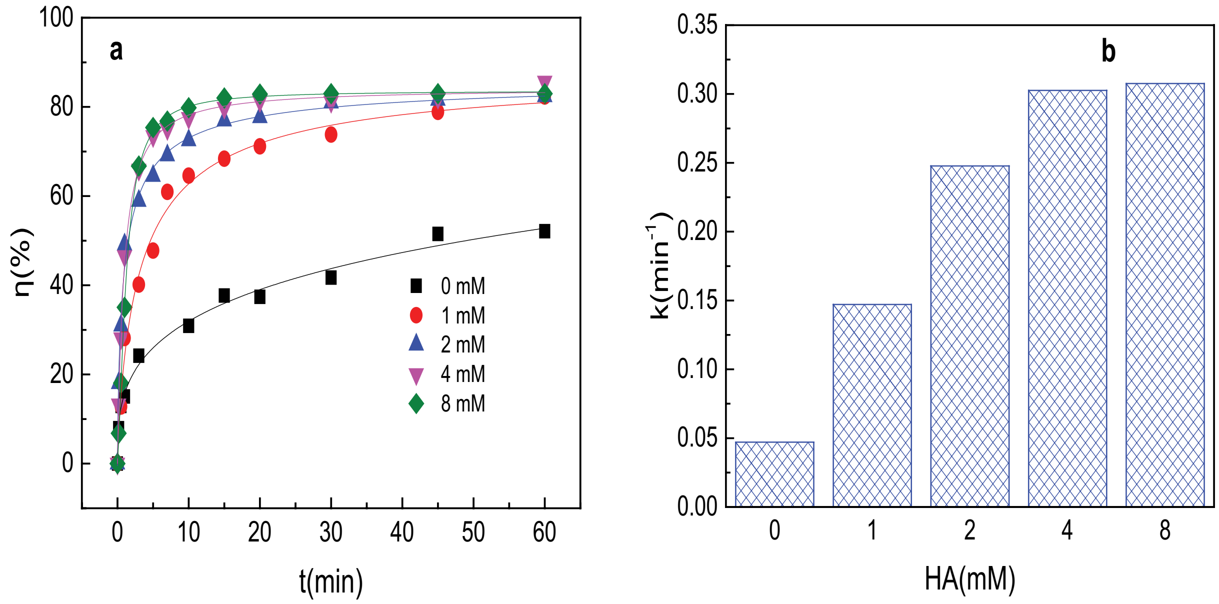

Fig. 2. (a) Tartrazine removal, (b) value of k for tartrazine removal, and (c) value of f at different HA concentrations. Reaction conditions: [Fe^{2+}] 0.1 mM; [H_2O_2] 2 mM; pH 4; [tartrazine] 200 mg L^{-1}.

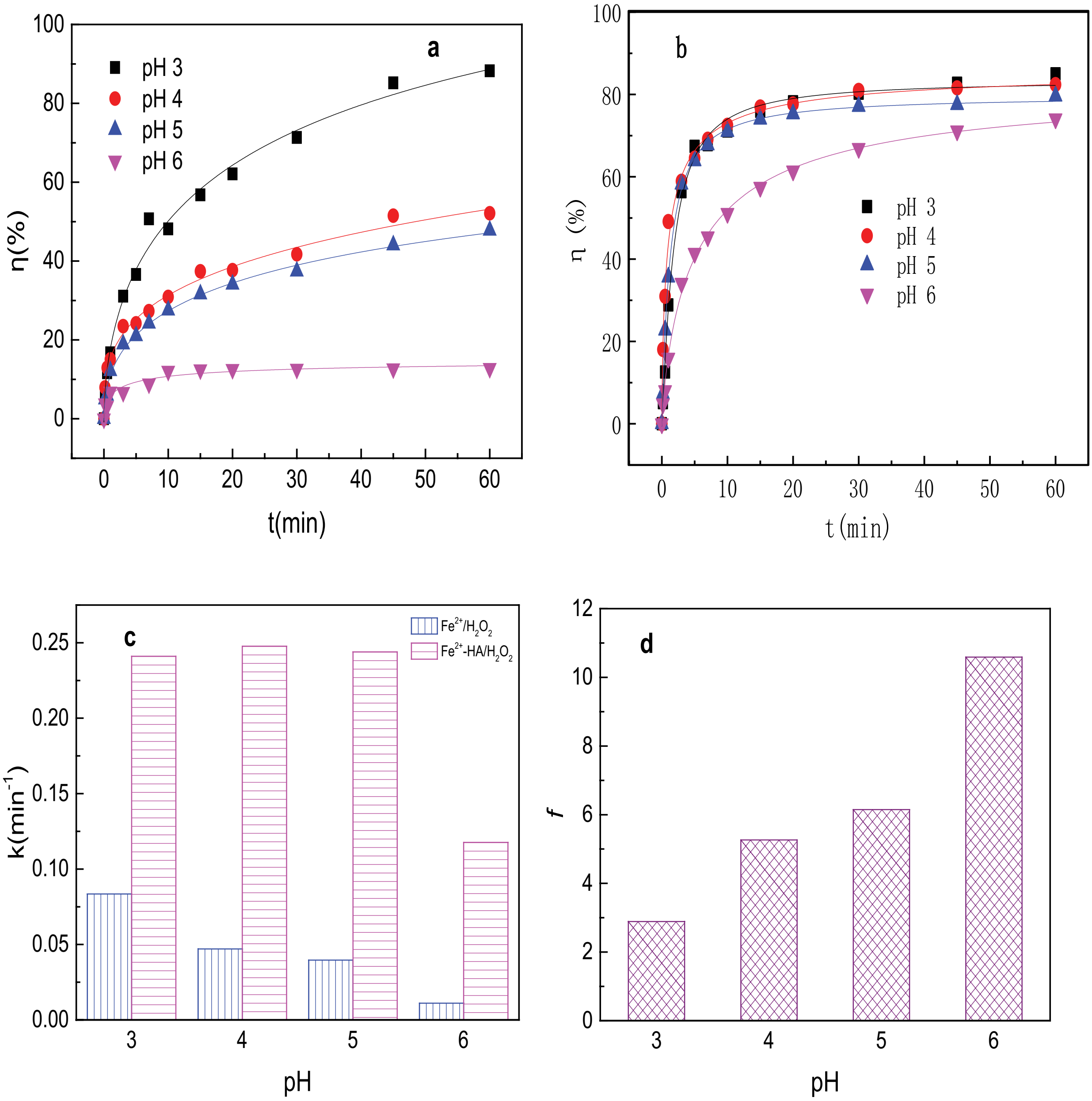

Fig. 3. (a) Tartrazine removal with the Fe^{2+}/H_2O_2 system, (b) tartrazine removal with the Fe^{2+}-HA/H_2O_2 system, (c) value of k for tartrazine removal with both systems, and (d) value of f at different initial pH values. Reaction conditions: [Fe^{2+}] 0.1 mM; [H_2O_2] 2 mM; [HA] 2 mM; [tartrazine] 200 mg L^{-1}.

increased significantly with increasing H_2O_2 concentration. The tartrazine removal was 70.3%, 82.4%, 89.4%, 94.3% and 95.9% when the H_2O_2 concentration was 1, 2, 4, and 8 mM at 16 mM. Moreover, the value of k increased from 0.212 to 0.418 min^{-1} when the H_2O_2 concentration increased from 1 to 8 mM, while the value of k decreased slightly to 0.409 min^{-1} when the H_2O_2 concentration further increased to 16 mM. The increase of H_2O_2 dosages evidenced a significant enhancement on the tartrazine removal efficiency which might because higher H_2O_2 concentration would induce higher $^{\bullet}OH$ concentration. The decrease in the value of k might be attributed to excessive H_2O_2 reacting with $^{\bullet}OH$ as shown in Eq. (8) [28]. Therefore, the optimal H_2O_2 dosage for removing tartrazine with the Fe^{2+}-HA/H_2O_2 system was 8 mM.

$$^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad (8)$$

3.3. Effect of inorganic ions and NOM

Inorganic anions are widely present in wastewaters and could significantly affect the removal efficiency of pollutants by the Fenton system. Therefore, common inorganic ions (such as SO_4^{2-}, Cl^- and HCO_3^-) were selected to evaluate their influence on the tartrazine removal with the Fe^{2+}/

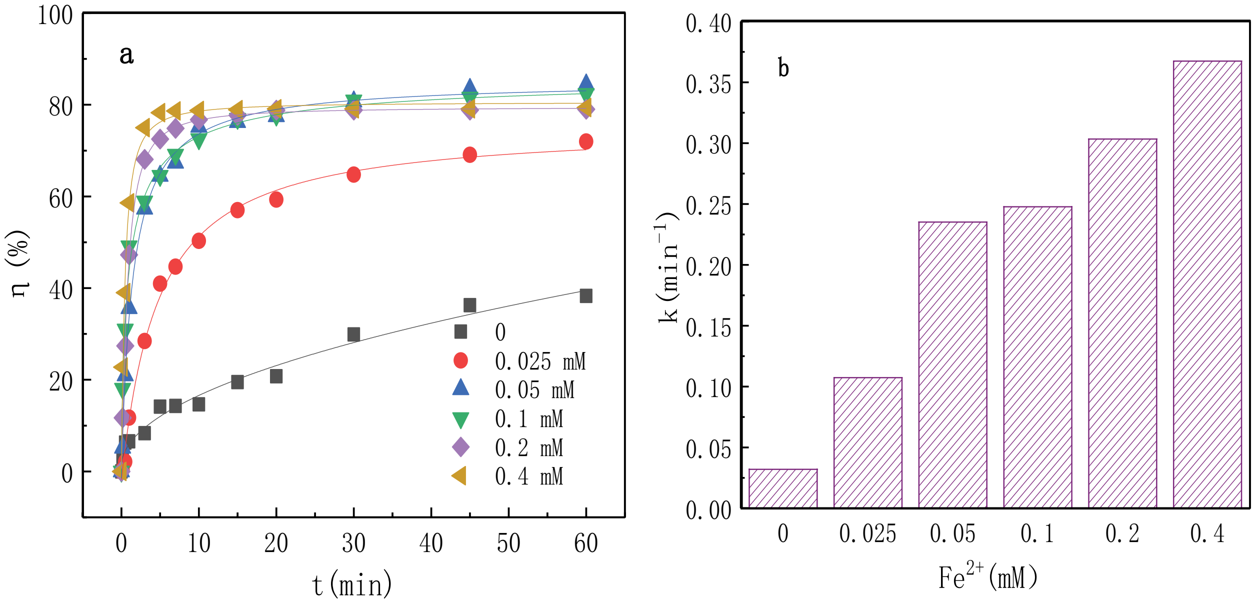

Fig. 4. (a) Tartrazine removal and (b) value of k for tartrazine removal at different Fe^{2+}concentrations. Reaction conditions: $[H_2O_2]$ 2 mM; pH 4; [HA] 2 mM; [tartrazine] 200 mg L^{-1}.

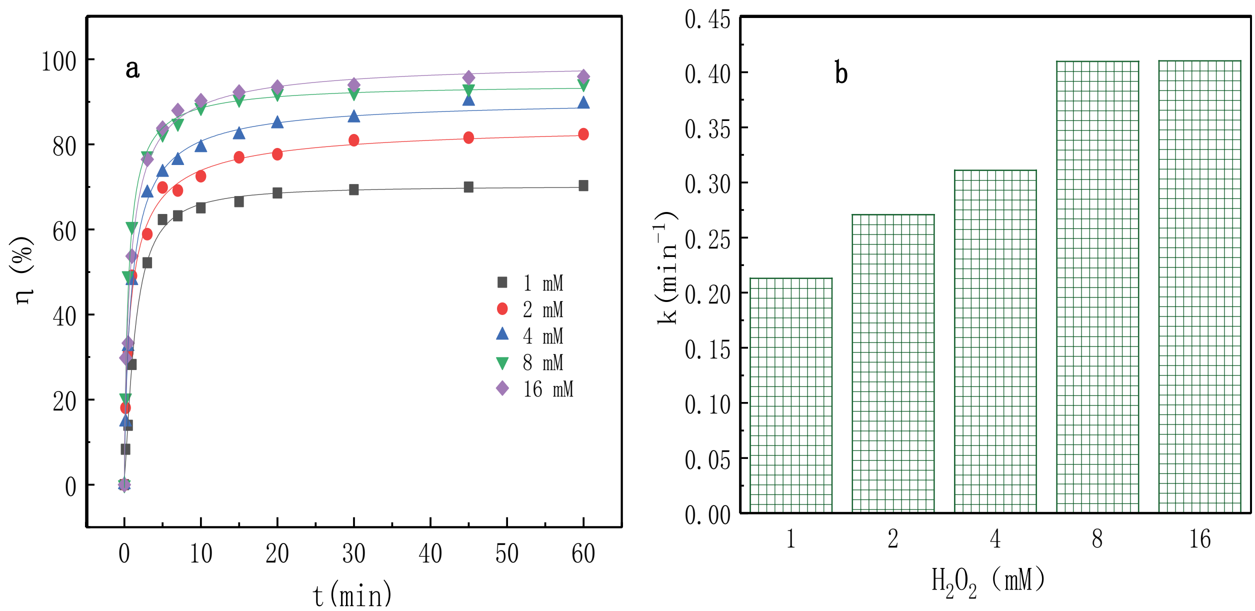

Fig. 5. (a) Tartrazine removal and (b) value of k for tartrazine removal at different H_2O_2 concentrations. Reaction conditions: $[Fe^{2+}]$ 0.1 mM; pH 4; [HA] 2 mM; [tartrazine] 200 mg L^{-1}.

H_2O_2 and Fe^{2+}-HA/H_2O_2 systems. As shown in Fig. 6a, the tartrazine removal with the Fe^{2+}/H_2O_2 system decreased significantly in the presence of inorganic ions. The tartrazine removal with the Fe^{2+}/H_2O_2 system decreased from 52.1% to 46.4%, 46.3%, and 35.8% in the presence of SO_4^{2-}, Cl^- and HCO_3^- within 60 min. The decrease in the tartrazine removal in the presence of inorganic ions might be due to the following reasons: (1) inorganic ions could react with the Fe ions, which would affect the distribution and reactivity of ferric species; (2) •OH radicals could also be scavenged by inorganic ions to form less reactive radicals (Eqs. (9)–(12)) [7]. HA could rapidly reduce Fe^{3+} to Fe^{2+}, thus accelerating the catalysis of H_2O_2 and enhancing the •OH production [25]. Higher production of •OH could better avoid the significantly decrease of the Fenton performance owing to some •OH radicals scavenged by inorganic ions forming less reactive radicals. Less Fe^{3+} could also prevent the reaction between Fe ions and inorganic ions preventing the effect of the distribution and reactivity of ferric species. As depicted in Fig. 6b, the tartrazine removal changed

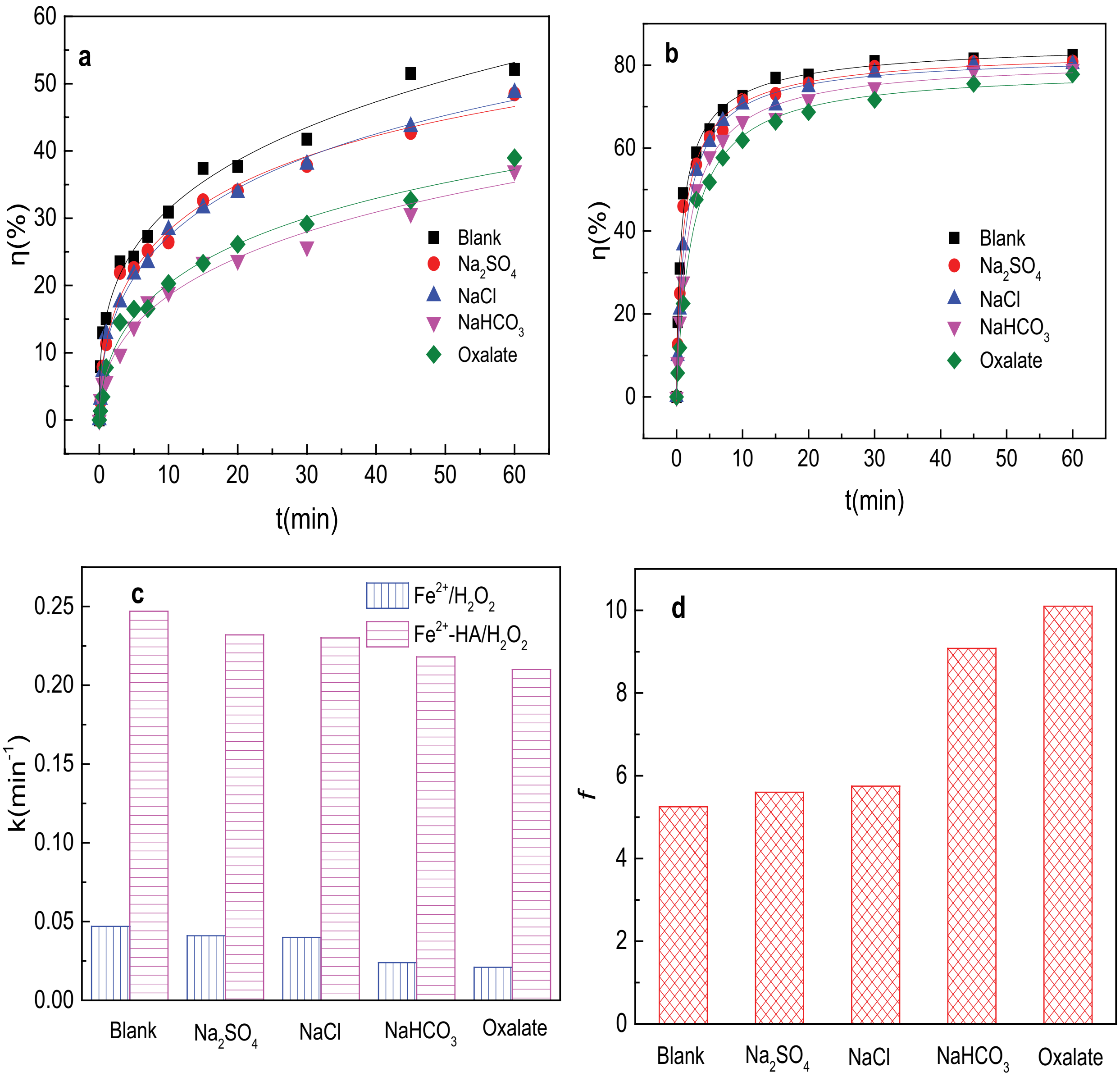

Fig. 6. Tartrazine removal in the presence of (a) Na_2SO_4, (b) NaCl, (c) $NaHCO_3$, (d) oxalate by the Fe^{2+}-HA/H_2O_2 system, and (e) value of k for tartrazine removal in the presence of different inorganic ions and Ox. Reaction conditions: [Fe^{2+}] 0.1 mM; [H_2O_2] 2 mM; pH 4; [HA] 2 mM; [tartrazine] 200 mg L^{-1}; [Na_2SO_4] 6 mM; [NaCl] 4 mM; [$NaHCO_3$] 0.5 mM; [Ox] 10 mg L^{-1}.

slightly in the presence of inorganic ions. The tartrazine removal with the Fe^{2+}-HA/H_2O_2 system only decreased from 82.4% to 81.6%, 80.9%, and 80.1% in the presence of SO_4^{2-}, Cl^- and HCO_3^- within 60 min. Moreover, as shown in Fig. 6c, the k values of removing tartrazine with the Fe^{2+}-HA/H_2O_2 system were also much larger than those with the Fe^{2+}/H_2O_2 system in the presence of different inorganic ions. As depicted in Fig. 6d, the value of f increased in the presence of different inorganic ions. These results demonstrated that the Fe^{2+}-HA/H_2O_2 process had a better tartrazine removal performance in the presence of inorganic ions.

$$Cl^- + {}^\bullet OH \rightarrow ClOH^{\bullet -} \quad (9)$$

$$Cl^- + ClOH^{\bullet -} \rightarrow Cl_2^{\bullet -} + OH^- \quad (10)$$

$$ClOH^{\bullet -} + H^+ \rightarrow Cl^\bullet + H_2O \quad (11)$$

$$HCO_3^- + {}^\bullet OH \rightarrow CO_3^{\bullet} + H_2O \quad (12)$$

NOM is widely present in wastewater and could be a competitor of tartrazine for $^\bullet$OH radicals. Thus, oxalates, as typical NOMs, were selected to explore the influence on tartrazine removal with the Fe^{2+}/H_2O_2 and Fe^{2+}-HA/H_2O_2 systems. As shown in Figs. 6a and b, tartrazine removal within 60 min decreased from 52.1% to 36.4% with the Fe^{2+}/H_2O_2 system but only decreased from 82.4% to 79.2% with the Fe^{2+}-HA/

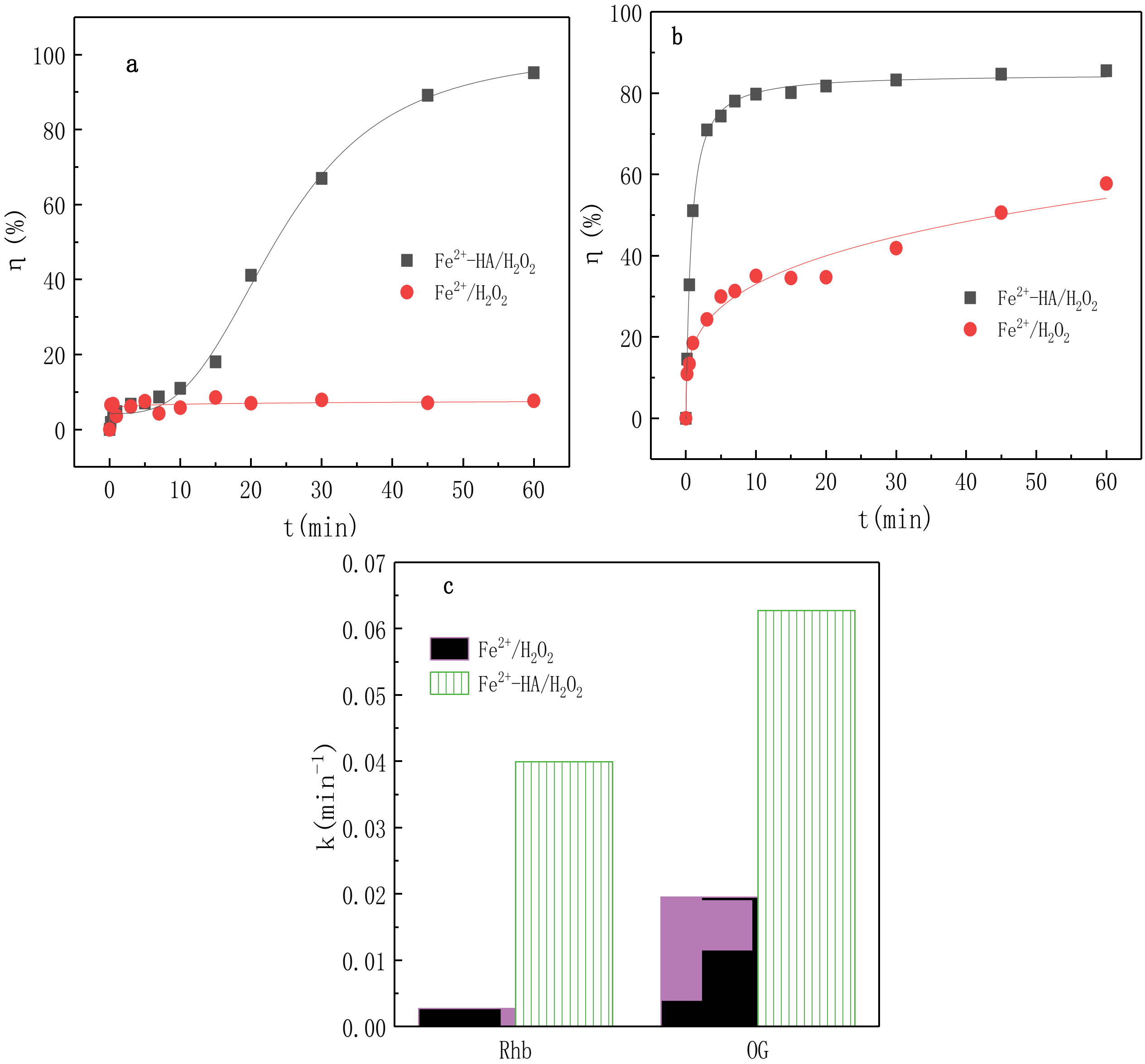

Fig. 7. (a) RhB removal with different systems, (b) OG removal with different systems, and (c) value of *k* for RhB and OG removal with different systems. Reaction conditions: [Fe^{2+}] 0.1 mM; [H_2O_2] 2 mM; pH 4; [HA] 2 mM; [RhB] 200 mg L^{-1}; [OG] 200 mg L^{-1}.

H_2O_2 system. The values of k for removing tartrazine with the Fe^{2+}-HA/H_2O_2 system were also much larger than those with the Fe^{2+}/H_2O_2 system, and the value of f also increased from 5.3 to 10.1 in the presence of oxalate. Therefore, the Fe^{2+}-HA/H_2O_2 process had a better performance for removing tartrazine in the presence of NOM.

3.4. Fe^{2+}-HA/H_2O_2 process employed for various organic pollutants

The Fe^{2+}-HA/H_2O_2 process-induced an improvement in the tartrazine removal, so it was reasonable to test whether this process would have the same effect on the removal of various refractory contaminants. We chose RhB and OG as examples. As shown in Fig. 7a, similar to the case of tartrazine removal, only 8.6% RhB could be removed within 60 min with the Fe^{2+}/H_2O_2 system, while 95.2% RhB could be removed within 60 min with the Fe^{2+}-HA/H_2O_2 system. As shown in Fig. 7b, only 57.8% OG could be removed within 60 min with the Fe^{2+}/H_2O_2 system, while 72.5% OG could be removed within only 10 min. Similarly, as shown in Fig. 7c, the value of k for removing RhB and OG with the Fe^{2+}-HA/H_2O_2 system (0.040 and 0.062 min^{-1}) was also much higher than that of the Fe^{2+}/H_2O_2 system (0.002 and 0.019 min^{-1}). Therefore, the Fe^{2+}-HA/H_2O_2 process could remove a wide range of organic pollutants and significantly improved the performance of the Fe^{2+}/H_2O_2 process.

4. Conclusion

HA was adopted to enhance the performance of the Fe^{2+}/H_2O_2 process for removing tartrazine. HA could accelerate the redox cycle of Fe^{3+}/Fe^{2+} and then enhanced the catalysis of H_2O_2 and the production of •OH for tartrazine removal. Tartrazine removal enhanced from 31.4% within 10 min with the Fe^{2+}/H_2O_2 system to 76.9% while HA was added into the Fe^{2+}/H_2O_2 system. Fe^{2+}-HA/H_2O_2 process could also broaden the working pH range from 3–4 to 3–6 for wastewater treatment. The pseudo-first-order constants of tartrazine removal by the Fe^{2+}-HA/H_2O_2 process were 2.9-, 5.3-, 6.2-, and 10.6-fold higher than that by the Fe^{2+}/H_2O_2 process at initial pH values of 3, 4, 5, and 6, respectively. Fe^{2+}-HA/H_2O_2 process could also keep better performance for tartrazine removal in the presence of inorganic ions and natural organic matter. Moreover, the values of k for removing RhB and OG with the Fe^{2+}-HA/H_2O_2 system (0.040 and 0.062 min^{-1}) were also much higher than those with the Fe^{2+}/H_2O_2 system (0.002 and 0.019 min^{-1}), indicating that the Fe^{2+}-HA/H_2O_2 process could remove a wide range of organic pollutants and significantly improved the performance of the Fe^{2+}/H_2O_2 process.

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