Hydroxylamine-facilitated removal of organic pollutants by the Fenton process

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Received 28 June 2020; Accepted 1 December 2020

Abstract

The traditional Fenton process cannot efficiently remove organic pollutants because of the low recycling efficiency of Fe²⁺. Hydroxylamine (HA) is a typical reducing agent that can accelerate the Fe²⁺ cycle. Thus, the HA-facilitated Fe²⁺/H₂O₂ removal of tartrazine was investigated. Only 31.4% tartrazine could be removed within 10 min with the Fe²⁺/H₂O₂ system, while 76.9% tartrazine could be removed with the Fe²⁺-HA/H₂O₂ system. The value of k for removing tartrazine with the Fe²⁺-HA/H₂O₂ system was 4.3-fold higher than that for removing tartrazine with the Fe²⁺/H₂O₂ system; the effect of various factors, such HA dosage (0–8 mM), initial pH (3–6), Fe²⁺ dosage (0–0.4 mM) and H₂O₂ dosage (1–16 mM), on the tartrazine removal with the Fe²⁺-HA/H₂O₂ system were also examined. The optimal HA, Fe²⁺, and H₂O₂ dosages were 4, 0.2 and 8 mM, respectively. The Fe²⁺-HA/H₂O₂ 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 Fe²⁺-HA/H₂O₂ process was better in the presence of inorganic ions and natural organic matter. Moreover, the Fe²⁺-HA/H₂O₂ process could remove a wide range of organic pollutants efficiently and significantly improved of the performance of the Fe²⁺/H₂O₂ process. Therefore, this study could improve our understanding of the effect of HA on promoting pollutant elimination with the Fe²⁺/H₂O₂ process.

Keywords: Hydroxylamine; Tartrazine; Fe²⁺/H₂O₂ 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 (Fe²⁺/H₂O₂) is an efficient and attractive process due to its simple operation, fast reaction rate, and environmental friendliness [8]. Hydroxyl radicals (·OH) can be generated by the reaction between Fe³⁺ and H₂O₂ (Eq. (1)) [9,10]. However, Fe³⁺ could not be recycled efficiently, leading to a low efficiency for pollutant removal because the reaction between Fe³⁺ and H₂O₂ (Eq. (2)) is much slower than that between Fe²⁺ and H₂O₂ (Eq. (1)) [11]. The poor recycling of Fe³⁺ also causes an accumulation of sludge and results in the requirements of a narrow working pH range (2.5–4) and high H₂O₂ dosage [11].

\[
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{OH}^- + \cdot\text{OH} \quad k = 76 \text{ M s}^{-1} \quad (1)
\]
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) Fe⁰ was substituted by heterogeneous catalysts, such as goethite (α-FeOOH) [14], zero-valent iron (ZVI, Fe⁰) [1], hematite (α-Fe₂O₃) [15], α-FeOOH/γ-Fe₂O₃ [16], Fe³⁺/Fe₂O₃ [17], Si–Al/α-FeOOH [18], and magnetite (Fe₃O₄) [19]. Heterogeneous catalysts could broaden the pH range, increase the recycling of Fe⁰ 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 ‘OH, for the target pollutants, thus inhibiting the pollutant removal efficiency.

Hydroxylamine (NH₂OH, HA) is a typical reducing agent that accelerates the redox cycle of Fe³⁺/Fe²⁺ (Eq. (3)) and enhances the catalysis of H₂O₂, and the production of ‘OH [23]. The addition of HA could also prevent the precipitation of Fe³⁺, 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@Fe₂O₃/H₂O₂ system [11], magnetically activated carbon/y-Fe₂O₃/H₂O₂ system [23], and CuFeO₂/H₂O₂ system [26] for the removal of various pollutants.

Fe³⁺ + NH₂OH → NH₂O⁻ + Fe²⁺ + H⁺ (3)

Therefore, the objectives of the present study were as follows: (1) investigate the performance of HA in terms of enhancing efficiency of the Fe²⁺/H₂O₂ system for tartrazine removal; (2) investigate the affecting factors, such as HA dosage, initial pH, Fe²⁺ dosage and H₂O₂ dosage, on tartrazine removal with the Fe²⁺-HA/H₂O₂ system; (3) investigate the effect of inorganic ions and natural organic matter (NOM) on tartrazine removal with the Fe²⁺-HA/H₂O₂ system; and (4) investigate the performance of the Fe²⁺-HA/H₂O₂ system for the removal of various pollutants.

2. Material and methods

2.1. Chemicals

Hydroxylamine, FeSO₄·7H₂O, H₂O₂ (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, Na₂SO₄ and NaHCO₃ 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, FeSO₄, tartrazine and H₂O₂ were added to the working solution. The initial pH value of the solution was adjusted with NaOH (0.1 mol L⁻¹) and H₂SO₄ (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 H₂O₂ concentration was detected by the potassium titanyl oxalate method at 400 nm. Fe³⁺ 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)).

η = \frac{C_0 - C}{C_0} \times 100 \tag{4}

\ln \frac{C}{C_0} = -kt \tag{5}

where k is the degradation rate, C₀ (mg L⁻¹) and C (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 k₁ and k₂ are the pseudo-first-order constants for removing pollutants with the Fe²⁺-HA/H₂O₂ and Fe³⁺/H₂O₂ systems, respectively.

3. Results and discussion

3.1. Tartrazine removal with various systems

As shown in Fig. 1a, the tartrazine removal with the H₂O₂, HA/H₂O₂, Fe²⁺/H₂O₂ and Fe³⁺-HA/H₂O₂ systems were compared. Only 2.8% tartrazine could be removed by H₂O₂ oxidation alone, demonstrating that H₂O₂ alone could not efficiently remove tartrazine. Fe²⁺ could catalyze H₂O₂ and then produce ‘OH; thus, 52.1% tartrazine could be removed within 60 min with the Fe²⁺-H₂O₂ system. HA could also catalyze H₂O₂ and 38.3% tartrazine could be removed within 60 min with the HA/H₂O₂ system. HA could also accelerate the redox cycle of Fe³⁺/Fe²⁺, thus improving the efficiency of Fe³⁺/H₂O₂ system, and 76.9% tartrazine could be removed within only 10 min with the Fe³⁺-HA/H₂O₂ system. Moreover, as shown in Fig. 2b, the tartrazine removal rate with the Fe²⁺-/HA/H₂O₂ system (0.247 min⁻¹) was much higher than that with the Fe³⁺/H₂O₂ system (0.047 min⁻¹).

The Fe³⁺ ion concentration played a critical role in pollutant removal with the Fenton system. Thus, the
concentration of Fe\(^{2+}\) ions was determined in both the Fe\(^{2+}/\)H\(_2\)O\(_2\) and Fe\(^{2+}\)-HA/H\(_2\)O\(_2\) systems. As depicted in Fig. 1c, the concentration of Fe\(^{2+}\) ions in the Fe\(^{2+}\)-HA/H\(_2\)O\(_2\) system was much higher than that in the Fe\(^{2+}/\)H\(_2\)O\(_2\) system. After 1 min of reaction, the concentration of Fe\(^{2+}\) ions was 0.084 mM in the Fe\(^{2+}\)-HA/H\(_2\)O\(_2\) system, but it was only 0.008 mM in the Fe\(^{2+}/\)H\(_2\)O\(_2\) system. A higher Fe\(^{2+}\) concentration could accelerate the catalysis of H\(_2\)O\(_2\) and induce faster H\(_2\)O\(_2\) catalysis, enhances the generation of \(\cdot\)OH, ultimately leading to higher tartrazine removal. As shown in Fig. 1d, the rate of the H\(_2\)O\(_2\) catalysis in the Fe\(^{2+}\)-HA/H\(_2\)O\(_2\) system was much faster than that in the other systems. Therefore, Fe\(^{2+}\) could accelerate the redox cycle of Fe\(^{3+}/\)Fe\(^{2+}\), thereby increasing the Fe\(^{2+}\) concentration, inducing a faster H\(_2\)O\(_2\) catalysis rate and accelerating \(\cdot\)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\(_2\)O\(_2\) catalysis and enhancing the generation of \(\cdot\)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\(_2\)O\(_2\) 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...
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 $\text{Fe}^{3+}/\text{Fe}^{2+}$. 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 $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ and $\text{Fe}^{2+}$-HA/$\text{H}_2\text{O}_2$ 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 $\text{Fe}^{2+}$-HA/$\text{H}_2\text{O}_2$ 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 $\text{Fe}^{2+}$-HA/$\text{H}_2\text{O}_2$ 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 $\text{Fe}^{3+}$, thus kept the good performance for tartrazine removal at nearly neutral pH in $\text{Fe}^{2+}$-HA/$\text{H}_2\text{O}_2$ system. Meanwhile, as illustrated in Fig. 3d, the pseudo-first-order constant of the tartrazine removal by the $\text{Fe}^{2+}$-HA/$\text{H}_2\text{O}_2$ process was 2.9-, 5.3-, 6.2-, and 10.6-fold higher than that of the tartrazine removal by the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ process at initial pH values of 3, 4, 5, and 6, respectively. Therefore, the $\text{Fe}^{2+}$-HA/$\text{H}_2\text{O}_2$ process could broaden the working pH range from 3–4 to 3–6 for wastewater treatment.

3.2.3. $\text{Fe}^{2+}$ dosage

The $\text{Fe}^{2+}$ concentration determines the rate of removing pollutants with the Fenton system; thus, the tartrazine removal was conducted with the $\text{Fe}^{2+}$-HA/$\text{H}_2\text{O}_2$ system at different $\text{Fe}^{2+}$ concentrations (0–0.4 mM). As depicted in Fig. 4a, HA could catalyze $\text{H}_2\text{O}_2$ to remove tartrazine, and 38.3% tartrazine could be removed within 60 min without $\text{Fe}^{2+}$ addition. The tartrazine removal increased quickly with $\text{Fe}^{2+}$ 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 $\text{Fe}^{2+}$ concentration increased from 0 to 0.025, 0.05, 0.1, 0.2 and 0.4 mM. Higher $\text{Fe}^{2+}$ concentration could catalyze $\text{H}_2\text{O}_2$ 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 $\text{Fe}^{2+}$ according to Eq. (7) [27]. Therefore, the optimal $\text{Fe}^{2+}$ dosage for removing tartrazine with the $\text{Fe}^{2+}$-HA/$\text{H}_2\text{O}_2$ system was 0.2 mM.

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

3.2.4. $\text{H}_2\text{O}_2$ dosage

The $\text{H}_2\text{O}_2$ concentration is a significant factor in the Fenton system because it is directly related to the concentration of $\cdot \text{OH}$, and therefore, the effect of the initial $\text{H}_2\text{O}_2$ concentration (1–16 mM) on the tartrazine removal was investigated. As illustrated in Fig. 5a, the tartrazine removal...
increased significantly with increasing \( \text{H}_2\text{O}_2 \) concentration. The tartrazine removal was 70.3%, 82.4%, 89.4%, 94.3% and 95.9% when the \( \text{H}_2\text{O}_2 \) 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 \( \text{H}_2\text{O}_2 \) concentration increased from 1 to 8 mM, while the value of \( k \) decreased slightly to 0.409 min\(^{-1}\) when the \( \text{H}_2\text{O}_2 \) concentration further increased to 16 mM. The increase of \( \text{H}_2\text{O}_2 \) dosages evidenced a significant enhancement on the tartrazine removal efficiency which might because higher \( \text{H}_2\text{O}_2 \) concentration would induce higher \( \cdot \text{OH} \) concentration. The decrease in the value of \( k \) might be attributed to excessive \( \text{H}_2\text{O}_2 \) reacting with \( \cdot \text{OH} \) as shown in Eq. (8) [28]. Therefore, the optimal \( \text{H}_2\text{O}_2 \) dosage for removing tartrazine with the \( \text{Fe}^{2+}-\text{HA/}\text{H}_2\text{O}_2 \) system was 8 mM.

\[
\cdot \text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^* \tag{8}
\]

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 \( \text{SO}_4^{2-} \), \( \text{Cl}^- \) and \( \text{HCO}_3^- \)) were selected to evaluate their influence on the tartrazine removal with the \( \text{Fe}^{2+}/ \)
H₂O₂ and Fe²⁺-HA/H₂O₂ systems. As shown in Fig. 6a, the tartrazine removal with the Fe²⁺/H₂O₂ system decreased significantly in the presence of inorganic ions. The tartrazine removal with the Fe²⁺/H₂O₂ system decreased from 52.1% to 46.4%, 46.3%, and 35.8% in the presence of SO₄²⁻, Cl⁻ and HCO₃⁻ 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 Fe³⁺ to Fe²⁺, thus accelerating the catalysis of H₂O₂ 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 Fe³⁺ 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
slightly in the presence of inorganic ions. The tartrazine removal with the Fe²⁺-HA/H₂O₂ system only decreased from 82.4% to 81.6%, 80.9%, and 80.1% in the presence of SO₄²⁻, Cl⁻ and HCO₃⁻ within 60 min. Moreover, as shown in Fig. 6c, the k values of removing tartrazine with the Fe²⁺-HA/H₂O₂ system were also much larger than those with the Fe²⁺/H₂O₂ 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 Fe²⁺-HA/H₂O₂ process had a better tartrazine removal performance in the presence of inorganic ions.

\[
\text{Cl}^- + \text{'OH} \rightarrow \text{ClO}^- \quad (9)
\]

\[
\text{ClO}^- + \text{'OH} \rightarrow \text{Cl}^- + \text{OH}^- \quad (10)
\]

\[
\text{ClO}^- + \text{H}^- \rightarrow \text{Cl}^- + \text{H}_2\text{O} \quad (11)
\]

\[
\text{HCO}_3^- + \text{'OH} \rightarrow \text{CO}_3^- + \text{H}_2\text{O} \quad (12)
\]

NOM is widely present in wastewater and could be a competitor of tartrazine for 'OH radicals. Thus, oxalates, as typical NOMs, were selected to explore the influence on tartrazine removal with the Fe²⁺/H₂O₂ and Fe²⁺-HA/H₂O₂ systems. As shown in Figs. 6a and b, tartrazine removal within 60 min decreased from 52.1% to 36.4% with the Fe²⁺/H₂O₂ system but only decreased from 82.4% to 79.2% with the Fe²⁺-HA/H₂O₂ system.
H₂O₂ system. The values of \( k \) for removing tartrazine with the Fe²⁺-HA/H₂O₂ system were also much larger than those with the Fe²⁺/H₂O₂ system, and the value of \( f \) also increased from 5.3 to 10.1 in the presence of oxalate. Therefore, the Fe²⁺-HA/H₂O₂ process had a better performance for removing tartrazine in the presence of NOM.

3.4. Fe²⁺-HA/H₂O₂ process employed for various organic pollutants

The Fe²⁺-HA/H₂O₂ 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 Fe²⁺/H₂O₂ system, while 95.2% RhB could be removed within 60 min with the Fe²⁺-HA/H₂O₂ system. As shown in Fig. 7b, only 57.8% OG could be removed within 60 min with the Fe²⁺/H₂O₂ 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 Fe²⁺-HA/H₂O₂ system (0.040 and 0.062 min⁻¹) was also much higher than that of the Fe²⁺/H₂O₂ system (0.002 and 0.019 min⁻¹). Therefore, the Fe²⁺-HA/H₂O₂ process could remove a wide range of organic pollutants and significantly improved the performance of the Fe²⁺/H₂O₂ process.

4. Conclusion

HA was adopted to enhance the performance of the Fe²⁺/H₂O₂ process for removing tartrazine. HA could accelerate
the redox cycle of Fe$^{3+}$/Fe$^{2+}$ and then enhanced the catalysis of H$_2$O$_2$ and the production of OH$^-$ for tartrazine removal. Tartrazine removal enhanced from 31.4% within 10 min with the Fe$^{2+}$/H$_2$O$_2$ system to 76.9% while HA was added into the Fe$^{2+}$/H$_2$O$_2$ system. Fe$^{2+}$/HA/H$_2$O$_2$ 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$^{3+}$/HA/H$_2$O$_2$ process were 2.9–, 5.3–, 6.2–, and 10.6-fold higher than that by the Fe$^{2+}$/H$_2$O$_2$ process at initial pH values of 3, 4, 5, and 6, respectively. Fe$^{2+}$/HA/H$_2$O$_2$ 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$_2$O$_2$ system (0.040 and 0.062 min$^{-1}$) were also much higher than those with the Fe$^{2+}$/H$_2$O$_2$ system (0.002 and 0.019 min$^{-1}$), indicating that the Fe$^{2+}$/HA/H$_2$O$_2$ process could remove a wide range of organic pollutants and significantly improved the performance of the Fe$^{2+}$/H$_2$O$_2$ process.

Acknowledgment

This study was financially supported by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

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