Tris–Co(II)–H$_2$O$_2$ System-Mediated Durative Hydroxyl Radical Generation for Efficient Anionic Azo Dye Degradation by Integrating Electrostatic Attraction

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Supporting Information

**ABSTRACT:** The development of simple Fenton/Fenton-like systems with durative hydroxyl radical (·OH) generation characteristics is significant to rapid organic pollutant degradation and cost-effective water treatment. In this study, a tris(hydroxymethyl)aminomethane (Tris)-incorporated Co(II)–H$_2$O$_2$ Fenton-like system has been successfully constructed for efficient Sunset Yellow (SY, a typical anionic azo dye) degradation under alkaline conditions. The mechanism of the enhanced degradation consists of two parts: first, the Tris–Co(II) complex triggers the durative generation of highly oxidized hydroxyl radicals; second, electrostatic attraction between SY and the Tris–Co(II) complex shortens the radical–SY interaction time and facilitates the degradation of SY. With the introduction of Tris to this proposed system, the decolorization rate of SY can be increased from 37.0 to 98.0% after 50 min and efficient SY degradation with a high total organic carbon removal efficiency (>59.0%) is achieved under a wide initial pH from 8.7 to 12.0. Moreover, the universality of the designed system for anionic azo dye degradation is verified with reactive red and congo red.

**INTRODUCTION**

Fenton/Fenton-like systems that produce highly oxidized hydroxyl radicals (·OH), have been widely applied in the degradation of organic contaminants.$^{1–5}$ However, conventional Fenton/Fenton-like systems only generate ·OH in a very short time, which restricts the degradation efficiency.$^6$ This is mainly due to the fast reaction rate between hydrogen peroxide (H$_2$O$_2$) and divalent transition metal ions (e.g., Fe(II) or Co(II)).$^{7,8}$ Thus, the durative generation of ·OH is of significance to further improve the performance of Fenton/Fenton-like systems. Toward this goal, a few systems with persistent ·OH production characteristics have been exploited by integrating other techniques.$^{9–14}$ For example, with the introduction of the electrochemical technique, consistent generation of ·OH over a long period has been reported.$^{15,16}$ Undoubtedly, these methods require specific setups and/or reaction conditions and are highly energy-intensive. Therefore, it is still appealing to explore a simple, efficient, and cost-effective method to generate ·OH continuously.

As is known, the chemical coordination of transition metal ions usually decreases their redox potentials and facilitates the trivalent/divalent conversion.$^{17,18}$ For instance, Tang et al. have demonstrated that the Fe(III)–ethylenediamine tetra-acetic acid (EDTA) chelating complex could catalyze H$_2$O$_2$ to generate ·OH efficiently in comparison to Fe(III) only.$^{19}$ The key role of the introduced chelating agents is to facilitate the conversion of trivalent transition metal ions to their divalent forms, which subsequently promotes the continuous generation of ·OH. Recently, we discovered that the redox potential of Co(III)/Co(II) can be greatly reduced using tris(hydroxymethyl)aminomethane (Tris) as the chemical chelator.$^{20}$ As a consequence, durative and effective generation of ·OH is observed. Utilizing Tris–Co(II) as the catalyst, efficient sterilizing and long-lasting chemical lights have been realized.$^{20,21}$ Owing to the excellent durative ·OH generation property, we speculate that this system might be promising to achieve efficient degradation of organic contaminants.
It is generally accepted that electrostatic attraction between organic contaminants and catalysts promotes the approach of generated *OH and benefits the complete oxidation and thereby increases the total organic carbon (TOC) removal efficiency. In this study, as a proof-of-concept, we explored a facile Tris–Co(II)–H₂O₂ Fenton-like system for efficient Sunset Yellow (SY, a typical anionic azo dye) degradation. The enhanced SY degradation is based on the fact that the Tris–Co(II) catalyst promotes the durable generation of *OH and that the strong electrostatic attraction between SY and the Tris–Co(II) catalyst facilitates the approach of *OH to SY. The efficiency of the proposed Fenton-like SY degradation system toward the initial pH was investigated. In addition, the degradation pathway was also investigated with liquid chromatography mass spectrometry (LC–MS). Furthermore, the universality of this system to other anionic azo dyes was validated by evaluating the degradation of reactive red and congo red.

**EXPERIMENTAL SECTION**

**Chemicals.** Sunset Yellow (SY) was purchased from Beijing lark technology Co., Ltd (Beijing, China). Tris (hydroxymethyl) aminomethane (Tris) was purchased from Beijing Solarbio Science & Technology Co., Ltd (Beijing, China). Cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O), hydrogen peroxide (H₂O₂, 30%, V/V), NaOH, HNO₃, dimethyl sulfoxide (DMSO), pyridine, glacial acetic acid, methylbenzene, n-butyl alcohol, and ethylenediaminetetraacetic acid (EDTA) disodium dihydrate salt were obtained from Beijing Chemical Reagent Company (Beijing, China). Fast Blue BB salt was purchased from Shanghai Yuan Ye Biological Chemical Reagent Company (Tianjin, China). Thiourea and nitro blue tetrazolium chloride (NBT) were obtained from Beijing Technology Co., Ltd (Shanghai, China). Sodium azide (NaN₃) was purchased from Tianjin Fuchen Chemical Reagent Company (Tianjin, China). Basic red, reactive red, and congo red were obtained from Shanghai Macklin Biochemical Co., Ltd (Shanghai, China). All chemicals were used directly without further purification. Ultrapure water (18.2 MΩ) from a Millipore system was used in all experiments. H₂O₂ stock solutions were prepared by diluting 30% H₂O₂. The stock solution of Co(II) with a concentration of 10.0 mmol/L was prepared by dissolving Co(NO₃)₂·6H₂O in ultrapure water directly. The concentrations of Tris and SY were 1.0 mol/L and 1.0 g/L, respectively. The initial pH values of degradation solutions were adjusted with HNO₃ or NaOH to investigate the pH influence on the SY degradation efficiency. At regular intervals of 5 min, the absorption of the degradation solution was measured using a UV-2401 PC spectrophotometer. The absorbance was used to determine the concentration of SY through the Beer–Lambert law. Similarly, the SY degradations in the Co(II)–H₂O₂, Tris–H₂O₂, Tris–Co(II), or only H₂O₂ systems were investigated according to the same procedure. Degradation of other azo dyes was performed with the same procedure by changing SY to other azo dyes without the change of the concentration.

**RESULTS AND DISCUSSION**

**Tris–Co(II)–H₂O₂ Fenton-Like System-Promoted Degradation of SY.** As a starting point, the degradation of SY in the Co(II)–H₂O₂ Fenton-like system without and with Tris was investigated. Figure 1 shows the degradation curves of SY versus time at an initial pH of 9.6 under various conditions. The decolorization rate of the SY solution with only H₂O₂ was negligible even after 50 min of reaction. Similarly, the decolorization rates of the SY solution in the presence of the Tris–H₂O₂ or Tris–Co(II) system with the same reaction time could also be ignored, suggesting that the Fenton-like system only works with both Co(II) and H₂O₂. With the simultaneous introduction of Co(II) and H₂O₂ degradation of
SY was observed with a decolorization rate of 37.0% within 50 min. Interestingly, it became 98.0% upon introducing Tris into the system, suggesting that Tris–Co(II) chelating complex plays an important role in SY degradation in the Co(II)–H₂O₂ Fenton-like system.

Our studies also showed that the degradation of SY in the Tris–Co(II)–H₂O₂ system was affected by the Tris concentration and initial solution pH. We then conducted a systematic study to optimize the conditions. According to Figure S1A, the SY degradation rate increased when the Tris concentration increased from 0 to 3 mM. However, further increase of Tris led to a slight decrease of the SY degradation rate. A possible reason is that with the increased Tris concentration can efficiently accelerate the Co(III)/Co(II) cycle, thereby increasing the production of *OH, which facilitates the degradation of SY.34 The slight decrease of the SY degradation rate at higher Tris concentrations might be attributed to the competitive consumption of *OH by excess Tris.25,26 Therefore, the degradation rate first increased and then decreased upon increasing the Tris concentration. Compared to the Fenton system, the Co(II)-mediated Fenton-like system shows higher activity under alkaline conditions based on previous reports.37 Thus, the initial solution pH values from 7.5 to 12.0 were considered. The degradation rate showed an initial increase and then a slight decrease upon increasing the solution pH, and the best reaction pH was 9.6. (Figure S1B) It is well-known that the generation of *OH from the Fenton-like reaction (Co(II)–H₂O₂) is promoted under alkaline conditions.28,29 As shown in Figure S1B, the degradation rate displayed an increase from pH 7.5 to 10.5. Nevertheless, it was decreased when the pH value was higher than 10.5. It is worth noting that H₂O₂ is easily decomposed into H₂O and O₂ in a strong alkaline solution (pH > 10.5),30 resulting in a diminished degradation rate. On the other hand, we calculated the stability constant of the Tris–Co(II) complex by spectrophotometry:31

\[
K = \frac{X}{(a - X)(b - nX)}
\]  

(1)

where \(K\) is the stability constant of the Tris–Co(II) complex, \(X\) is the concentration of the Tris–Co(II) catalyst at equilibrium (mol/L), \(n\) is the coordination number of the Tris–Co(II) catalyst (the stoichiometry of the Tris–Co(II) catalyst between Co(II) and Tris was determined by the continuous variation method to be 1:3),32 \(a\) is the concentration of Co(II) (mol/L), and \(b\) is the concentration of Tris (mol/L). As shown in Figure S2, the total concentrations of Co(II) and Tris were maintained as 0.01 mol/L (red) and 0.005 mol/L (black). When the absorbance is 0.6, the concentrations of Co(II) and Tris of the two solution compositions are \(a₁ = 1.3 \times 10^{-6} \text{ mol/L}\), \(b₁ = 8.7 \times 10^{-6} \text{ mol/L}\) and \(a₂ = 1.0 \times 10^{-6} \text{ mol/L}\), \(b₂ = 4.0 \times 10^{-6} \text{ mol/L}\), respectively. The value of \(K\) obtained from eq 1 is 1.87 × 10^{14}. When the Tris–Co(II) complex is in equilibrium, it is calculated that free [Co²⁺] in the solution is 2 × 10^{-12} mol/L. According to literature surveys,33 the \(K_{sp}\) of Co(OH)₂ is 2.5 × 10^{-16}. The value of free [OH⁻] was calculated to be 10^{-2} mol/L. Therefore, Co(OH)₂ will precipitate at pH = 12, which inhibits the generation of reactive oxygen species. Taken together, the highest degradation rate is achieved when the Tris concentration is 3 mM and the initial solution pH is 9.6. It is noticed that most of the SY (>95.0%) could be degraded within 50 min of reaction time at an initial pH from 9.6 to 12.0, indicating that this approach is remarkably capable for the treatment of printing and dyeing wastewaters, since the pH values of the wastewaters are always alkaline.34

Mechanism of Tris–Co(II) Catalyst-Enhanced Degradation of SY. To prove that the Tris–Co(II) catalyst promoted SY degradation, the mineralization efficiency of SY under optimal conditions was investigated by a TOC analysis.35,36 Notice that the introduction of Tris can dramatically enhance the TOC value of the solution; the TOC background from Tris needs to be excluded. To obtain the mineralization rate of SY with the Tris–Co(II)–H₂O₂ system, the TOC values of the Tris–Co(II)–H₂O₂ solution with and without SY during reaction were accordingly recorded. The difference between these two values stands for the net TOC of SY. The initial TOC value of Tris was 137.3 mg/L, while only 2.3% of it was mineralized within 80 min (Figure S3). To achieve a high mineralization efficiency, continuous addition of H₂O₂ three times was conducted (Figure 2A). Despite this, the TOC removal efficiency of the SY–Co(II)–H₂O₂ solution without or with Tris increased with the progress of the reaction. However, it was much faster in the SY–Tris–Co(II)–H₂O₂ solution. The mineralization efficiency was 11.0% in the SY–Co(II)–H₂O₂ solution; however, it became 59.4% in the SY–Tris–Co(II)–H₂O₂ solution. The dramatic TOC variation revealed that the Tris–Co(II) catalyst-promoted SY degradation might be attributed to the high mineralization efficiency. Such a high TOC removal efficiency of our proposed degradation system is better than those of some previously reported works using small molecules as chelators.37 In addition, the production of sulfate was largely enhanced with the addition of Tris. According to Figure 2B, the sulfate concentrations in the SY–Co(II)–H₂O₂ and SY–Tris–Co(II)–H₂O₂ solutions after reaction were 3.6 and 10.6 µM, respectively. Since sulfate can only generate from the oxidation of the sulfonic group of SY, the higher the sulfate concentration, the higher the degradation efficiency.38 It should be referred that nitrate was not considered in ion chromatograph measurements because cobalt nitrate was used as a Co(II) source. Meanwhile, the concentrations of HCOOH and CH₃COOH were 213.9 and 38.8 µM upon adding Tris, which may originate from the degradation of Tris. These small molecules are nontoxic and biodegradable, and do not need to be further treated.

Although *OH is the major component in Fenton-like reactions, other reactive oxygen species including superoxide anion (O₂⁻) and singlet oxygen (¹O₂) also exist. To find out
as to which one is responsible for SY degradation, three reactive oxygen species scavengers (thiourea for \( \cdot \text{OH} \), superoxide dismutase (SOD) for \( O_2^{**} \), and \( \text{NaN}_3 \) for \( 1\text{O}_2 \)) were investigated.\(^{39–42} \) As shown in Figure S4, the addition of \( \text{NaN}_3 \) showed negligible inhibition to SY degradation, suggesting that \( 1\text{O}_2 \) is not involved in the direct degradation process. In contrast, thiourea and SOD caused distinct

suppressions to SY degradation (Figure 3), indicating that \( \cdot \text{OH} \) and \( O_2^{**} \) are responsible for the effective SY degradation. In comparison to SOD, thiourea led to \( \sim 90.0\% \) inhibition of SY degradation, implying that \( \cdot \text{OH} \) is the major species that degrades SY.

To understand how Tris affects the production of \( \cdot \text{OH} \) and \( O_2^{**} \) in the Co(II)–H\(_2\)O\(_2\) Fenton-like system process, we quantified \( \cdot \text{OH} \) in the absence and presence of Tris using a classical Babbs method based on a previous report.\(^{43} \) The reaction between DMSO and \( \cdot \text{OH} \) can produce methane sulfonic acid (MSA), a stable compound. Then, MSA interacts with Fast Blue BB salt and produces yellow diazosulfone, which leads to an increase of the characteristic absorption band at 425 nm. The absorbance at 425 nm was measured with an interval of 5 min and was used to represent the amount of produced MSA for each period. According to Figures 4A and S5, the production of \( \cdot \text{OH} \) in Co(II)–H\(_2\)O\(_2\) system mostly occurred in the initial 5 min. In contrast, \( \cdot \text{OH} \) was unremittingly generated within 50 min in the presence of Tris. The total content of \( \cdot \text{OH} \) in the Co(II)–H\(_2\)O\(_2\) and Tris–Co(II)–H\(_2\)O\(_2\) systems within a 50 min period were calculated to be 1.3 and 3.4 \( \mu \)mol, respectively. These results indicated that Tris not only promotes the continuous generation but also the yield of \( \cdot \text{OH} \). Accordingly, the production of \( O_2^{**} \) was quantified using the NBT method based on the absorbance decrease at 259 nm.\(^{44,45} \) As shown in Figures 4B and S6, the yield of \( O_2^{**} \) in the Tris–Co(II)–H\(_2\)O\(_2\) system is much higher than that in the Co(II)–H\(_2\)O\(_2\) system. Interestingly, the production of \( \cdot \text{OH} \) is proportional to the yield of \( O_2^{**} \), suggesting that \( O_2^{**} \) may be involved in the \( \cdot \text{OH} \) production process. It is reported that \( O_2^{**} \) acts as a reductant in the Fenton-like system, which is important for the redox-active Co(III)/Co(II) conversion.\(^{36} \) A similar role of \( O_2^{**} \) was found in other Fenton-like systems. Sun et al. have reported that \( O_2^{**} \) can reduce Fe(III)-chelates to Fe(II)-chelates in the Fe(III)–NTA–Mn\(^{2+} \) Fenton-like system and subsequently increase the generation rate of \( \cdot \text{OH} \) from the reaction between Fe(II)–NTA complexes and H\(_2\)O\(_2\).\(^{46} \) We thus speculate that the generated \( O_2^{**} \) would accelerate the reduction of the Tris–Co(III) complex to the Tris–Co(II) complex and facilitate the

Figure 3. Time profiles of the SY degradation in the Tris–Co(II)–H\(_2\)O\(_2\) system upon adding various concentrations of thiourea (A) and SOD (B).

Figure 4. Time-dependent production of \( \cdot \text{OH} \) (A) and \( O_2^{**} \) (B) in Co(II)–H\(_2\)O\(_2\) (black histogram) and Tris–Co(II)–H\(_2\)O\(_2\) (red histogram) systems. (C) SY degradation in the Co(II)–H\(_2\)O\(_2\) system (1), adding \( 6 \times 10^{-8} \) mol Co(II) every 10 min in the Co(II)–H\(_2\)O\(_2\) system (2) and adding \( 6 \times 10^{-8} \) mol Co(II) every 5 min in the Co(II)–H\(_2\)O\(_2\) system (3) and Tris–Co(II)–H\(_2\)O\(_2\) system (4). (D) Influence of \( O_2^{**} \) to \( \cdot \text{OH} \) formation in the Tris–Co(II)–H\(_2\)O\(_2\) system.

Scheme 1. Schematic Illustration of the Tris–Co-catalyst-Promoted Continuous Generation of \( \cdot \text{OH} \) in the Co(II)–H\(_2\)O\(_2\) Fenton-like System

with a fixed interval also enhanced the degradation efficiency of SY (Figure 4C), further proving the importance of the Co(II) content to the generation of \( \cdot \text{OH} \) and the following SY degradation. Additionally, this speculation was verified by measuring \( \cdot \text{OH} \) production in the presence of NBT. As illustrated in Figure 4D, the addition of a low concentration of NBT significantly inhibited \( \cdot \text{OH} \) production due to the consumption of \( O_2^{**} \).

In addition to the continuous production of \( \cdot \text{OH} \), shortening the reaction time between \( \cdot \text{OH} \) and the organic pollutant is also an efficient strategy to enhance the degradation of organic pollutants.\(^{47,48} \) The \( \zeta \)-potentials of Tris–Co(II) complexes and SY were measured to be 7.7 and \(-14.8 \) mV, respectively (Figure 5A). The opposite charges make them easily get close and form a complex due to the strong electrostatic attraction. Undoubtedly, the \( \zeta \)-potential value became \(-2.72 \) mV when mixing Tris–Co(II) complexes and SY together. The decreased \( \zeta \)-potential suggests the formation of Tris–Co(II)–SY complexes. Therefore, the
increasing cycle number (Figure S10A), which is due to the As expected, the degradation rate of SY decreased with the and the mixture of SY and the Tris hinders the approach of Co(II) complex, which shows electrostatic repulsion to SY and S7), mainly because of the negative charge of the EDTA improving the degradation e interaction.49 We thus investigated the SY degradation by adding various concentrations of KCl.

Figure 5. (A) ζ-Potentials of the Tris−Co(II) complex (1), SY (2), and the mixture of SY and the Tris−Co(II) complex (3). (B) Time profiles of the SY degradation in the Tris−Co(II)−H2O2 system upon adding various concentrations of KCl.

reaction time between •OH and SY is largely shortened, which improves the degradation efficiency. As is known, the high ionic strength environment can reduce the electrostatic interaction.50 We thus investigated the SY degradation by adding an electrolyte (KCl). As shown in Figure 5B, the SY degradation efficiency decreased with increasing KCl concentration, further validating the importance of forming Tris−Co(II)−SY complexes. To better understand the importance of the electrostatic attraction between the Tris−Co(II) complex and SY, SY degradation by EDTA−Co(II) complexes was also investigated. It was found that the decolorization rate of SY solution in the EDTA−Co(II)−H2O2 system is much slower than that in the Tris−Co(II)−H2O2 system (Figure S7), mainly because of the negative charge of the EDTA−Co(II) complex, which shows electrostatic repulsion to SY and hinders the approach of •OH. Similarly, the degradation of basic red (a cationic azo dye) in the Tris−Co(II)−H2O2 system within 50 min was negligible at pH 9.6. Interestingly, the degradation efficiency could be greatly enhanced by increasing the solution pH value (Figure S8), which diminishes the electrostatic repulsion between basic red and the Tris−Co(II) complex and facilitates their osculation. To further identify the interaction, FT-IR spectra were analyzed. As shown in Figure S9, the S=O stretch band shifted from 1027 to 1039 cm⁻¹, which is due to the electrostatic interaction between the anionic sulfonic group and the positive Tris−Co(II) complex. These results generally demonstrate the essential role of the electrostatic attraction between organic dyes and the Tris−Co(II) complex for the effective degradation of organic dyes.

Taken together, the Tris−Co(II) catalyst-promoted SY degradation can be divided into two parts: Tris decreases the redox potential and facilitates the Co(III)/Co(II) conversion and continuous generation of •OH; the strong electrostatic attraction between Tris−Co(II) and SY shortens the reaction time and enhances the degradation efficiency.

Cyclic Degradation of SY by the Tris−Co(II)−H2O2 System. As mentioned in our investigations, only a slight decomposition of Tris during the degradation of SY occurred, suggesting the preservation of the Tris−Co(II) complex. Therefore, we hypothesized that the Tris−Co(II) complex can be used for cyclic degradation of SY upon re-addition of H2O2. As expected, the degradation rate of SY decreased with the increasing cycle number (Figure S10A), which is due to the continuously reduced Tris during the degradation process. However, the high degradation efficiency (>90%) of SY was realized even after five cycles (Figure S10B). These results indicated the effective cyclic degradation capability of the Tris−Co(II) complex toward SY in the presence of H2O2.

Degradation Pathway of SY in the Tris−Co(II)−H2O2 System. According to the above results, the introduction of Tris into the Co(II)−H2O2 Fenton-like system can greatly enhance the degradation of SY. To understand the degradation pathway, the degradation intermediates of SY were investigated through the LC−MS technique. As shown in Figure 6A, five components in the LC chromatogram were observed with retention times of 0.76, 1.05, 1.23, 1.57, and 2.83 min, respectively. The possible structures of these components were identified from the MS data (Figure S11 and Table S1).50,51 On the basis of MS results of previous reports, these five components were characterized as 4-hydroxybenzenesulfonate ion (1), hydroxylated derivative of 4-hydroxybenzenesulfonate ion (2), hydroxylated derivative of 1,4,6-trihydroxy-2-naphthalenesulfonate ion (3), 1,4-naphthoquinone (4), and cyclopentanecarboxylic acid (5), respectively. These compounds also appeared in SY degradation with the Co(II)−H2O2 Fenton-like system, indicating that the introduction of Tris did not change the degradation pathway. In addition, the continuous changes of corresponding UV−vis absorption spectra of SY solution were recorded to further research the degradation pathway. SY has three characteristic absorption peaks around 482, 314, and 230 nm, respectively (Figure 6B).50 The absorption peak in the visible light region (482 nm) is assigned to the π−π* transition of the azo group. However, the absorption peaks in the ultraviolet region (314 and 230 nm) belong to the n−π* transition of the naphthalene ring and azo bond, respectively.52 As shown in Figure 6B, the absorbance at 482 nm gradually decreased and finally disappeared during the reaction, indicating the cleavage of the azo bond. Despite the absorbance decrease in the UV region, the incomplete disappearance of the absorption peaks suggests that the aromatic ring compounds still exist within 50 min, which is consistent with the LC−MS results.

On the basis of all of the above results and previous reports, we proposed a possible degradation pathway of SY in the Tris−Co(II)−H2O2 system (Scheme 2), which is very similar to that in the Co(II)−H2O2 system. First, the process is started by the cleavage of the N=N bond of SY, which results in the generation of 4-aminobenzenesulfonate and 5-nitro-6-hydroxy-2-naphthalenesulfonate. Because of the high reactivity of these two intermediates, their mass signals were not observed, which is consistent with previously reported researches.50,51 Second, the oxidation of 4-aminobenzenesulfonate occurs and produces compound 1 and compound 2. Meanwhile, •OH attacks the substitution of nitroso groups on the naphthalene ring and
produces compound 3. Then, the hydroxylated derivative was oxidized to form compound 4 and subsequently compound 5. Eventually, \( ^* \text{OH} \) oxidizes benzene compounds and cyclopentane compounds to generate environment-friendly small-molecule organic acids and other inorganic species including CO\(_2\), H\(_2\)O, sulfate, etc.

**Universality of Anionic Azo Dye Degradation with the Tris–Co(II)–H\(_2\)O\(_2\) System.** The high SY degradation efficiency of the Tris–Co(II)–H\(_2\)O\(_2\) system suggests that this system might be capable of degradation of other anionic azo dyes. The universality of the proposed Tris–Co(II)–H\(_2\)O\(_2\) system was evaluated with another two anionic azo dyes, reactive red and congo red. As shown in Figure 7, both reactive red and congo red exhibited an extremely low degradation efficiency (< 20.0%) within 60 min reaction time in the Co(II)–H\(_2\)O\(_2\) system. However, they became 80.0% and 99.0% in the Tris–Co(II)–H\(_2\)O\(_2\) system. These results suggested that the Tris–Co(II)–H\(_2\)O\(_2\) system is expandable for promoting the degradation of other anionic azo dyes. In comparison to SY, both reactive red and congo red showed a lower degradation rate. A possible reason is that the additional amine-motif in reactive red and congo red reduces their negative charge and subsequently weakens the interaction between the dye and the Tris–Co(II) complex. This assumption was proved by \( \zeta \)-potential measurements of reactive red and congo red. The \( \zeta \)-potentials of reactive red and congo red were \(-9.4 \) and \(-3.6 \) mV, which are lower than that of SY. Meanwhile, the degradation rate of reactive red was faster than that of congo red, which is consistent with the \( \zeta \)-potential results. Therefore, we can claim that the Tris–Co(II)–H\(_2\)O\(_2\) system can be applied for the efficient degradation of anionic azo dyes.

**CONCLUSIONS**

In conclusion, we have proposed a simple Tris–Co(II)–H\(_2\)O\(_2\) system for effective SY degradation under alkaline conditions. The enhanced degradation efficiency is based on the integration of the Tris-promoted Co(III)/Co(II) conversion and the formation of the Tris–Co(II)–SY complex via strong electrostatic attraction, which facilitates the continuous generation of \( ^* \text{OH} \) and shortens the reaction time. The universality of the presented strategy is validated by the high degradation efficiencies of other anionic azo dyes, reactive red and congo red. Our study demonstrates efficient organic contaminant degradation via the integration of durative generation of \( ^* \text{OH} \) and electrostatic attraction, and thus, new avenues for the design of highly effective systems for homogeneous and/or heterogeneous Fenton/Fenton-like degradation of organic pollutants or catalytic reaction based on a similar strategy may now be possible in the environmental and chemistry-related fields.
ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b02331.

Time profiles of the SY degradation with different Tris concentration or under different initial pH values (Figure S1); absorbance and composition Tris—Co(II) complex solution (Figure S2); retention time, structural formula and m/z value of SY degradation intermediates (Table S1) (PDF)

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Notes
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