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**DOI**
10.1016/j.jtice.2016.08.027

**Publication date**
2016

**Document Version**
Accepted author manuscript

**Published in**
Journal of the Taiwan Institute of Chemical Engineers

**Citation (APA)**
Liu, Z., Guo, Y., Shang, R., Fang, Z., Wu, F., & Wang, Z. (2016). A triple system of Fe(III)/sulfite/persulfate: Decolorization and mineralization of reactive Brilliant Red X-3B in aqueous solution at near-neutral pH values. *Journal of the Taiwan Institute of Chemical Engineers*, *68*, 162-168. https://doi.org/10.1016/j.jtice.2016.08.027

# A triple system of Fe(III)/sulfite/persulfate: Decolorization and mineralization of reactive Brilliant Red X-3B in aqueous solution at near-neutral pH values

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## Abstract

We report herein the use of ferric iron ($Fe^{3+}$) and sulfite ($SO_3^{2-}$) to activate persulfate ($S_2O_8^{2-}$). Decolorization and mineralization of reactive Brilliant Red X-3B (a model azo dye) by an Fe(III)/sulfite/persulfate triple system have been investigated in aqueous solutions. Initial pH and dissolved oxygen are important factors influencing X-3B decolorization in this system. The rapid decolorization process occurred in 30 min and about 85% of X-3B was decolorized in this triple system at initial pH 6.0. Moreover, about 66.4% of the TOC was removed through reaction for 36 h. The generation of $SO_4^{\bullet-}$ and $HO^{\bullet}$ were identified through radical quenching experiments and by electron spin resonance (ESR), which contributed to 61.1% and 28.9% of the oxidation process. Degradation products of X-3B were identified by LC-ESI-MS, and the degradation pathway was proposed. Furthermore, other organic pollutants, such as Orange II, metoprolol, imipramine, naproxen, estradiol, and amitriptyline, could also be efficiently degraded in this triple system. The results of the present work suggest that the Fe(III)/sulfite/persulfate triple system can be used for the rapid decolorization and partial mineralization of dyeing wastewater at near-neutral pH values.

*Keywords:* Decolorization; Ferric iron; Sulfite; Persulfate; Neutral pH

## 1. Introduction

An efficient method for chemical oxidation based on the sulfate radical ($SO_4^{\bullet-}$) has gained widespread attention. In recent decades, studies have investigated the application of $SO_4^{\bullet-}$ in the degradation of organic contaminants, such as dyes, pesticides, and antibiotics that are non-biodegradable in municipal wastewater treatment [1-4]. Persulfate ($S_2O_8^{2-}$, $E^0$=2.01V) is generally recognized as a strong oxidant when $SO_4^{\bullet-}$ ($E^0$=2.6V) is generated, and the $SO_4^{\bullet-}$ can be effectively activated by a variety of means such as UV irradiation, heat, alkaline pH, and so on [5-7]. Among these approaches, the addition of a transition metal appears to be the most viable way for achieving persulfate activation [8,9]. In this regard, Fe(II) and Fe(III) are the most commonly used metal activators due to their natural abundance in environmental media [10,11].

However, the traditional Fe(II)/persulfate system has several drawbacks, including scavenging of $SO_4^{\bullet-}$ by excessive Fe(II), rapid conversion of Fe(II) to Fe(III) [4,12], and a low efficiency of Fe(II) recovery, which result in the generation of voluminous iron sludge and restrict its practical application [11]. Thus, a significant decrease in degradation efficiency was observed with increasing pH, primarily due to the precipitation of iron at higher pH values [13-16]. To overcome these deficiencies, different approaches have been used to control Fe(II) depletion rate and relieve Fe(III) precipitation in related studies. The introduction of organic and inorganic ligands for iron is one of the most attractive methods to overcome these defects. Citric acid [17,18] and EDTA [11,19] have been the most commonly used ligands in the Fe(II)/persulfate process to prevent iron precipitation from aqueous solutions. However, it should be borne in mind that adding organic ligands to the system increases the total organic carbon in the solution, and therefore may cause environmental pollution and increase subsequent wastewater treatment costs.

In our previous work, we reported novel systems utilizing Fe(II)-sulfite and photo-Fe(II)-sulfite for the $SO_4^{\bullet-}$-mediated decolorization of Orange II [20-22]. As an inorganic ligand, sulfite can form stable $FeHSO_3^+/FeSO_3^+$ complexes with Fe(II) and Fe(III), and $SO_4^{\bullet-}$ can be simultaneously generated through a series of reactions [23-25]. By forming such complexes, sulfite enhances the solubility and stabilizes Fe(III) in aqueous solution at near-neutral pH and promotes Fe(III)/Fe(II) redox cycles. In addition, $Na_2SO_3$ is much more stable than $K_2S_2O_8$, and Fe(II)-sulfite is more environmentally friendly than systems containing $K_2S_2O_8$ [20]. Consequently, $Na_2SO_3$ has potential to replace $K_2S_2O_8$ in wastewater treatment. To the best of our knowledge, there has been only one report of the combined use of potassium persulfate and sodium sulfite, in which *N*-acryloyl morpholine was polymerized onto chitosan as a redox initiator [26]. Very few data are available concerning environmental conditions and reaction mechanisms in activating persulfate by the Fe(III)-sulfite complex.

In the present work, Fe(III)-sulfite complex has been used to activate persulfate and accelerate Fe(III)/Fe(II) redox cycles. Reactive Brilliant Red X-3B, a model azo dye, was chosen as a target contaminant. The aim of this study was to examine the decolorization and mineralization of X-3B by an Fe(III)/sulfite/persulfate triple system at near-neutral pH values. For this purpose, the effects of Fe(III) concentration, sulfite concentration, persulfate concentration, initial pH, and dissolved oxygen on the rapid decolorization process were investigated. Furthermore, total organic carbon (TOC) was analyzed to examine the extent of mineralization.

## 2. Materials and methods

### *2.1. Materials*

Reactive Brilliant Red X-3B (≥90%, structures provided in Table A1, Supporting Information) was supplied by Sinopharm Chemical Reagent Co., Ltd (52 Ningbo RD, Shanghai, China). Orange II, metoprolol, imipramine, naproxen, estradiol, and amitriptyline were also supplied by Sinopharm Chemical Reagent Co., Ltd. Ferric sulfate ($Fe_2(SO_4)_3$), sodium sulfite ($Na_2SO_3$), and potassium persulfate ($K_2S_2O_8$, ≥99.5%) were obtained from Wuhan Chemicals Corporation. NaOH and $H_2SO_4$ were obtained from Sinopharm Chemical Reagent Co., Ltd., and were used to adjust the pH of solutions. 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO) was from Sigma-Aldrich Co., China. *tert*-Butyl alcohol (TBA) and ethanol (EtOH) were obtained from Sinopharm Chemical Reagent Co., Ltd., and were used as scavengers of the radicals. All chemicals were of analytical reagent grade or of higher purity and were used without further purification. Doubly-distilled deionized water (Milli-Q) was used to prepare all solutions.

### *2.2. Oxidation Reaction*

All experiments were carried out in a 250 mL glass reactor with tubing to allow the bubbling of gas. Each solution was maintained under constant magnetic stirring at room temperature (293 ± 2 K). A certain amount of X-3B solution was mixed with Fe(III)-$Na_2SO_3$ solution. The initial pH was adjusted with dilute NaOH and $H_2SO_4$ as quickly as possible. The pH was measured using a pHS–3C meter and adjusted as needed. The reaction started when $K_2S_2O_8$ was added to the solution. At the same time, the pH was measured once again; the variation in pH after the addition of $K_2S_2O_8$ was less than 0.1 pH units. Aliquots of the solution were withdrawn at various intervals and measured on a spectrophotometer. The experiments were conducted in triplicate, and the variations are shown as error bars in the figures. The initial concentration of X-3B was 40 mg $L^{-1}$ in all of the experiments.

### *2.3. Analysis*

The concentrations of X-3B and Orange II were measured by means of a UV-3000 spectrophotometer at wavelengths of 540 and 485 nm, respectively. The calibration curve for the detection of X-3B is shown in Fig. A1 (supplementary data). The concentrations of metoprolol, imipramine, naproxen, estradiol, and amitriptyline were analyzed by means of a Shimadzu Essentia LC-15C HPLC system with an Agilent HC-C18 column (5 μm, 250 mm × 4.6 mm) [27-31]. The pH was measured using a pHS–3C meter and the dissolved oxygen (DO) concentration was measured by an HQ-10 DO meter. TOC analysis was performed on an Analytik Jena multi N/C 2100. DMPO was used as the spin-trapping agent in the ESR experiments. Detailed parameters and the experimental ESR procedure are provided in the Supporting Information Text A1. X-3B products were determined by LC-ESI-MS. Detailed parameters and the LC-ESI-MS analytical procedure are provided in the Supporting Information Text A2.

## 3. Results and discussion

### *3.1. Decolorization of X-3B by the Fe(III)/sulfite/persulfate triple system*

To assess the performance of the Fe(III)/sulfite/persulfate triple system, reactive Brilliant Red X-3B was chosen as a target contaminant, and its decolorization process was investigated. Fig. 1 shows the results of X-3B decolorization in different systems at near-neutral pH (6.0). It was found that no decolorization occurred merely in the presence of Fe(III), $Na_2SO_3$, $K_2S_2O_8$, or $Na_2SO_3/K_2S_2O_8$. The decolorization of X-3B was negligible in the Fe(III)/$K_2S_2O_8$ system because of the inability to activate $K_2S_2O_8$ and iron precipitation from the aqueous solution. In contrast, Fe(III)/sulfite, Fe(II)/persulfate, and Fe(III)/sulfite/persulfate systems were proved to be capable of inducing X-3B decolorization, among which the Fe(III)/sulfite/persulfate system was the most effective. More than 80% of the X-3B was decolorized within 30 min in this system, as compared to only 44.2% and 11.8%, respectively, in the Fe(III)/sulfite and Fe(II)/persulfate systems.

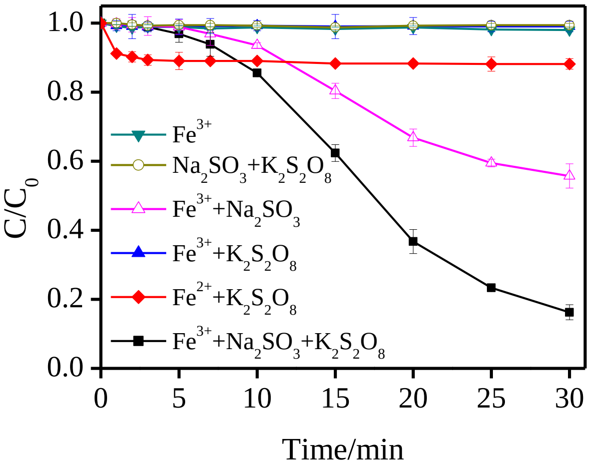


**Fig. 1** – Decolorization of X-3B by different systems at near-neutral pH values. Reaction conditions: $[X\text{-}3B]_0 = 40$ mg $L^{-1}$, $[Fe^{3+}]_0 = 0.1$ mmol $L^{-1}$, $[Na_2SO_3]_0 = 1$ mmol $L^{-1}$, $[PS]_0 = 2$ mmol $L^{-1}$, pH 6.0.

A summary of the reactions in the Fe(III)/sulfite/persulfate triple system is given in Table 1. There are two pathways to generate $SO_4^{\bullet-}$ in this triple system: Fe(III) firstly serves as a metal ion for the formation of $Fe^{III}SO_3^+$ complex with $SO_3^{2-}$ and as a radical initiator for $SO_3^{\bullet-}$ (eqs. 1 and 2), $SO_5^{\bullet-}$ (eq. 3), and $SO_4^{\bullet-}$ (eq. 4) with the generation of Fe(II) (eq. 2) [23]. Sequentially, Fe(II) can react with $S_2O_8^{2-}$ through a series of processes to produce $SO_4^{\bullet-}$ and $^{\bullet}OH$ (eqs. 8–12) (Scheme 1). The continuous generation of $SO_4^{\bullet-}$ and $^{\bullet}OH$ is largely subject to the redox cycling process of Fe(III)/Fe(II). The slow decolorization in the first 10 min can be explained by the fact that the slow decomposition of $FeSO_3^+$ limits the reaction rate in this system [20]. Any process that accelerates the Fe(III)/Fe(II) redox cycling will certainly be favorable for enhancing radical generation. In contrast, the Fe(III)/Fe(II) redox cycling process cannot be achieved in the Fe(II)/persulfate system, wherein the rapid conversion of Fe(II) to Fe(III) limits the ultimate oxidizing capability [32,33]. To the best of our knowledge, the $Fe^{III}SO_3^+$ complex is stable in the pH range 3.0–6.0, and this prevents the iron from precipitation at pH 6.0. Fig. A2 shows the UV/Vis spectra of Fe(III) (0.1 mmol $L^{-1}$), X-3B (40 mg $L^{-1}$), and a mixture of Fe(III) and X-3B. According to these UV/Vis spectra, the absorbance of the mixture of Fe(III) and X-3B was simply a superposition of their respective absorption spectra, suggesting that iron and X-3B did not form a complex in this work. Therefore, the Fe(III)/sulfite complex is a good alternative for activating persulfate in aqueous solution at near-neutral pH values.

**Table 1** – A summary of reactions in the Fe(III)/sulfite/persulfate triple system.

| Reactions | ($k$/M$^{-1}$s$^{-1}$) | | Refs. |
|---|---|---|---|
| $Fe^{3+} + HSO_3^{-} \leftrightarrow FeSO_3^{+} + H^{+}$ | $\log k = 2.45$ | (1) | [34] |
| $FeSO_3^{+} \rightarrow Fe^{2+} + SO_3^{\bullet-}$ | $k = 0.19\ s^{-1}$ | (2) | [35] |
| $SO_3^{\bullet-} + O_2 \rightarrow SO_5^{\bullet-}$ | $k = (1.1–2.5) \times 10^{9}$ | (3) | [36,37] |
| $SO_5^{\bullet-} + HSO_3^{-} \rightarrow SO_4^{2-} + SO_4^{\bullet-} + H^{+}$ | $k \approx 1.2 \times 10^{4}$ | (4) | [38] |
| $SO_5^{\bullet-} + HSO_3^{-} \rightarrow HSO_5^{-} + SO_3^{\bullet-}$ | $k < 3 \times 10^{5}$ | (5) | [39] |
| $2\ SO_5^{\bullet-} \rightarrow 2\ SO_4^{\bullet-} + O_2$ | $k = 10^{4} – 10^{8}$ | (6) | [39,40] |
| $2\ SO_5^{\bullet-} \rightarrow S_2O_8^{2-} + O_2$ | $k = 10^{7} – 10^{8}$ | (7) | [40] |
| $Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\bullet-}$ | $k = 2.7 \times 10^{1}$ | (8) | [41] |
| $SO_4^{\bullet-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-}$ | $k = 4.6 \times 10^{9}$ | (9) | [42] |
| $SO_4^{\bullet-} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{\bullet-}$ | $k = (6.1–6.3) \times 10^{9}$ | (10) | [43] |
| $SO_4^{\bullet-} + OH^{-} \rightarrow SO_4^{2-} + HO^{\bullet}$ | $k = (1.4–6.5) \times 10^{7}$ | (11) | [43] |
| $SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + H^{+} + HO^{\bullet}$ | $k = 1.1 \times 10^{1}$ | (12) | [43] |
| $HSO_3^{-} + H^{+} \leftrightarrow SO_2 + H_2O$ | $k = 6.2 \times 10^{4}$ | (13) | [44] |
| $SO_4^{\bullet-} + HSO_3^{-} \rightarrow SO_4^{2-} + SO_3^{\bullet-} + H^{+}$ | $k = 1.3 \times 10^{8} – 2.5 \times 10^{9}$ | (14) | [39,45] |

The good performance of this triple system was also successfully verified with other organic pollutants, such as Orange II, metoprolol, imipramine, naproxen, estradiol, and amitriptyline (Fig. A3). The degradation of imipramine, amitriptyline was 57.5% and 47.6% respectively. However, less than 30% of metoprolol, naproxen and estrodiol was decolorized in the Fe(III)/sulfite/persulfate triple system. It was found that this triple system is suitable for the selective removal of organic pollutants from mixed industrial wastewater. This feature implies that this triple system can potentially be applied in industrial wastewater treatment.

### *3.2. Effect of initial pH*

To understand the effect of initial pH on the X-3B decolorization process with this triple system, experiments were conducted at pH 2.0–7.0. The initial concentrations of Fe(III), $Na_2SO_3$, and $K_2S_2O_8$ were 0.1, 1, and 2 mmol $L^{-1}$, respectively. Fig. 2 shows that similar degrees of decolorization were achieved within 30 min at pH 3.0–6.0, albeit at different reaction rates, whereas the degradation of X-3B was significantly inhibited at pH 2.0 and 7.0. This can be explained by the fact that the effective concentration of $HSO_3^-$ decreased when the sulfur dioxide was formed at pH 2.0 (eq. 13) [44, 46], and this process sequentially influenced the generation of $FeSO_3^+$ complex and $SO_4^{\bullet-}$ (Eqs. 1 and 2). At pH 7.0, the free Fe(III) was completely precipitated and, therefore, the decrease in X-3B decolorization was largely due to the loss of Fe(III) activity.

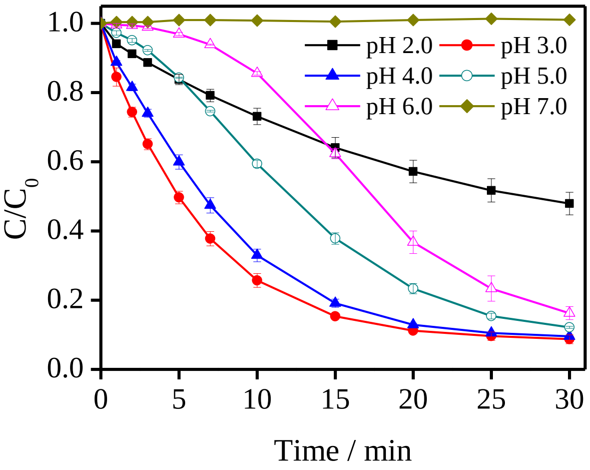


**Fig. 2** – Effect of pH on X-3B decolorization by Fe(III)/sulfite/persulfate triple system. Reaction conditions: $[X\text{-}3B]_0 = 40$ mg $L^{-1}$, $[Fe^{3+}]_0 = 0.1$ mmol $L^{-1}$, $[Na_2SO_3]_0 = 1$ mmol

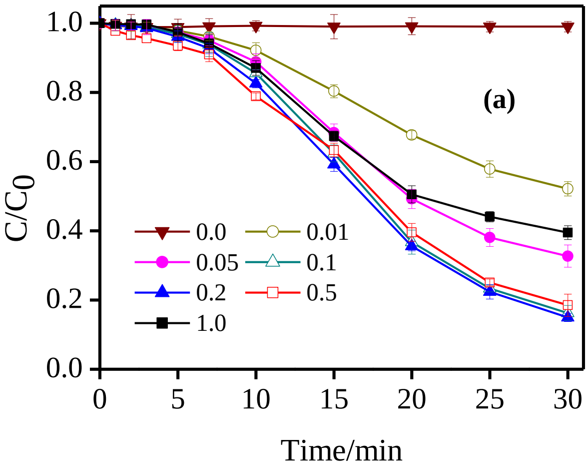
$L^{-1}$, $[PS]_0 = 2$ mmol $L^{-1}$.

In order to further elucidate this phenomenon, variations in pH during the reaction process were recorded and the results are shown in Fig. A4. pH decreased sharply from initial values of 4.0–6.0, and eventually stabilized at about 3.5. It was believed that the $H^+$ was generated through reactions (1), (4), and (12) [21], which are the main sources of hydrogen production. This may account for the similar decolorization efficiencies at pH 4.0–6.0. Although pH 3.0 and 4.0 proved to be optimal for X-3B decolorization, the initial near-neutral pH was more feasible for environmental applications. Therefore, all further experimental studies were carried out under near-neutral pH conditions.

As a control experiment, the decolorization process of X-3B under different pH conditions by the Fe(II)/persulfate system was also investigated (Fig. A5a). At pH 5.0 and 6.0, very limited decolorization rates were achieved, in stark contrast to the results with the Fe(III)/sulfite/persulfate triple system. The variation of DO was almost the same at different initial pH (Fig. A5b), which implied that the DO has no effect on the Fe(II)/persulfate system. Therefore, the variation of DO in triple system was caused by activation of sulfite. The pH was monitored during the reaction process, and no significant change was detected (Fig. A5c). The variation of pH was consistent with the decolorization of X-3B. It proved that the generation of $SO_4^{\bullet-}$ at near-neutral pH values was less than that at acid pH condition, as $H^+$ was a byproduct in the process of persulfate activation. Higher pH will clearly lead to iron precipitation and restrict practical application of the Fe(II)/persulfate system at near-neutral pH values.

### *3.3. Effects of Fe(III), $Na_2SO_3$, and $K_2S_2O_8$ concentrations*

X-3B decolorization at pH 6.0 in the presence of Fe(III), $Na_2SO_3$, and $K_2S_2O_8$ at various concentrations was evaluated. Fig. 3 shows that there were close correlations between decolorization efficiency and Fe(III), $Na_2SO_3$, and $K_2S_2O_8$ concentrations. It was observed that X-3B decolorization had a common tendency when the concentrations of these three reagents were changed. Firstly, the decolorization of X-3B was enhanced with increasing amounts of Fe(III), $Na_2SO_3$, and $K_2S_2O_8$ until an optimal dosage ratio was reached. Higher dosage of these three reagents led to steady decreases in the decolorization efficiency.



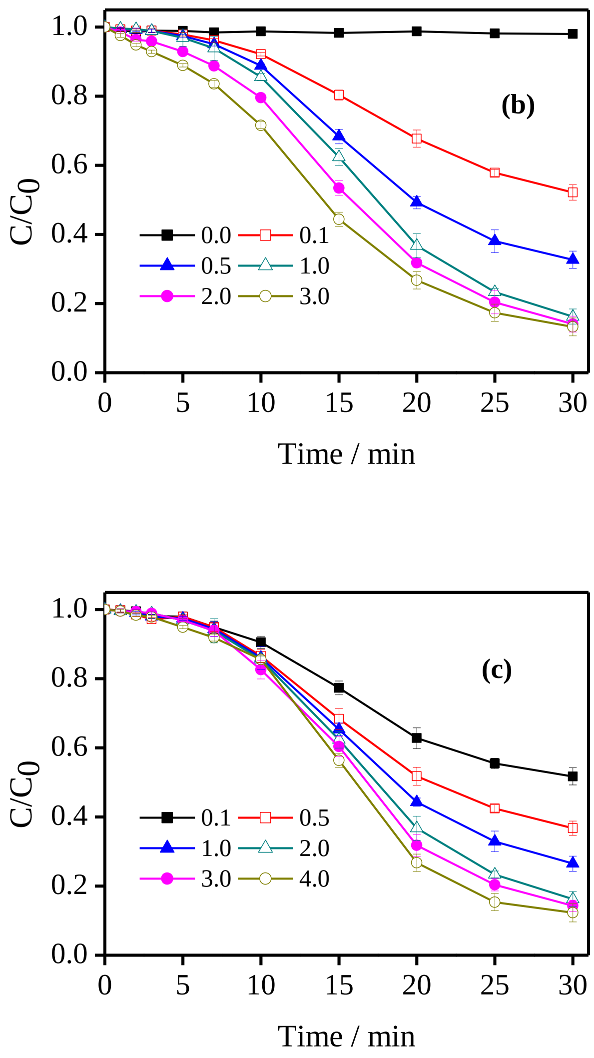


**Fig. 3** – Effects of Fe(III) (a), $Na_2SO_3$ (b), and $K_2S_2O_8$ (c) concentrations on X-3B decolorization by Fe(III)/sulfite/persulfate triple system. Reaction conditions: [X-3B] = 40 mg $L^{-1}$, pH 6.0, (a) $[Na_2SO_3]_0$ = 1 mmol $L^{-1}$, $[PS]_0$ = 2 mmol $L^{-1}$; (b) $[Fe^{3+}]_0$ = 0.1 mmol $L^{-1}$, $[PS]_0$ = 2 mmol $L^{-1}$; (c) $[Fe^{3+}]_0$ = 0.1 mmol $L^{-1}$, $[Na_2SO_3]_0$ = 1 mmol $L^{-1}$.

It should be noted that, when the concentrations of Fe(III), $Na_2SO_3$, and $K_2S_2O_8$ exceed the optimal dosage ratio, the excess reagents compete with X-3B for depletion the $SO_4^{\bullet-}$ radicals. Therefore, the presence of excess reagents slows down the formation of $SO_4^{\bullet-}$ radicals. In this triple system, iron is able to generate $SO_4^{\bullet-}$ radicals by the reaction with $HSO_3^-$ (eqs. 1–4) but also depletes $SO_4^{\bullet-}$ radicals from $S_2O_8^{2-}$ through eq. 9 [11]. Similarly, excess $S_2O_8^{2-}$ and $SO_3^{2-}$ react with $SO_4^{\bullet-}$ radicals through eqs. 10 and 14, respectively [4, 20], and thereby reduce the decolorization efficiency of the triple system.

### *3.4. Effect of dissolved oxygen*

The effect of oxygen on X-3B decolorization in the Fe(III)/sulfite/persulfate triple system at pH 6.0 was investigated by bubbling oxygen or nitrogen into the reaction solution. In the presence of oxygen, X-3B was decolorized more rapidly, whereas in the absence of oxygen (bubbling nitrogen), the decolorization was strongly retarded (Fig. 4a). To our knowledge, DO is the oxidant involved in $SO_5^{\bullet-}$ generation (eq. 3), and is therefore indirectly responsible for the decolorization of X-3B. Variations in DO concentration were monitored to provide indirect proof during the bubbling oxygen process. It was observed that DO underwent a rapid depletion in the first 2 min, and then recovered during the following 30 min (Fig. A6). Moreover, the DO depletion rates vary at different initial pH. As shown in Fig. 4b, the depletion rates of dissolved oxygen decreased in the order pH 7.0 < pH 6.0 < pH 5.0 < pH 4.0 < pH 3.0. This trend was consistent with that in X-3B decolorization. It was found that at pH 3.0–7.0, the lowest DO concentration was always observed at 1–3 min; thereafter, reoxygenation slowly increased the DO concentration. The raise of DO concentration is due to both the aeration of the reaction solution and the spontaneous generation of oxygen through eqs. 6 and 7. Therefore, this result indicates that DO influences the decolorization rates in the Fe(III)/sulfite/persulfate triple system.

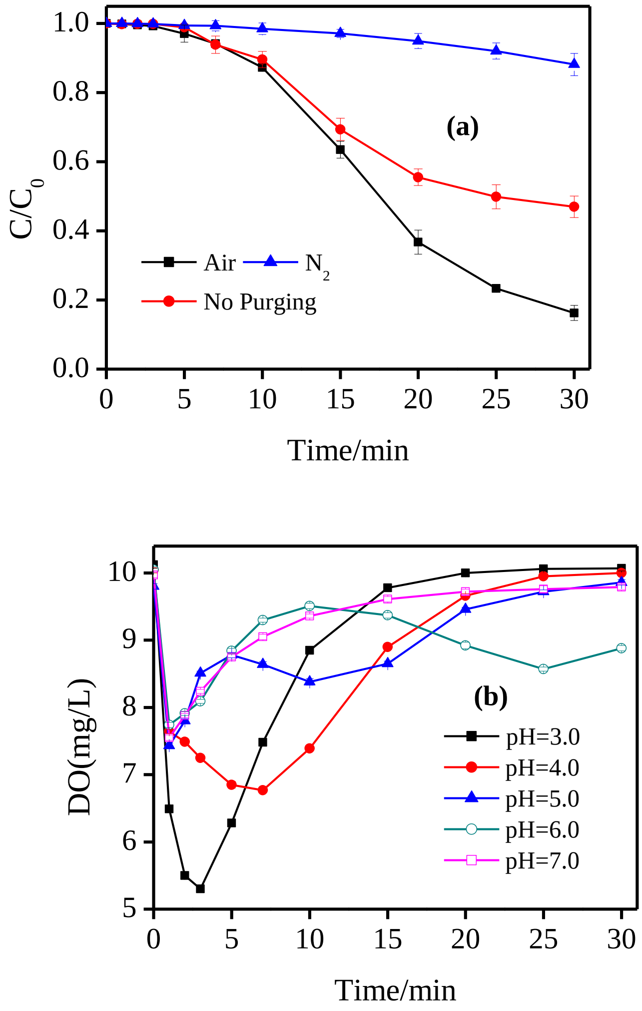


**Fig. 4** – Effect of oxygen on the decolorization of X-3B at pH 6.0 (a), variations of DO concentration at different initial pH (b) by Fe(III)/sulfite/persulfate triple system. Reaction conditions: [X-3B] = 40 mg $L^{-1}$, $[Fe^{3+}]_0$ = 0.1 mmol $L^{-1}$, $[Na_2SO_3]_0$ = 1 mmol $L^{-1}$, $[PS]_0$ = 2 mmol $L^{-1}$.

### *3.5. Identification of the radicals*

DMPO was selected as the spin-trapping agent to identify the involved reactive radicals ($^{\bullet}OH$ and $SO_4^{\bullet-}$) by measuring the signals of DMPO−$^{\bullet}OH$ adducts and DMPO−$SO_4^{\bullet-}$ adducts, respectively [47]. Fig. A7 shows that no radicals could be generated in DMPO + Fe(III), DMPO + persulfate, DMPO + sulfite systems because no peaks were observed. The intensity of the DMPO radical adduct signals was identified in the Fe(II)–PS and Fe(III)–PS–sulfite processes. The observed characteristic signals were presumed to be a combination of DMPO−$^{\bullet}OH$ adduct (with $a_N = a_H = 14.9$ G) and DMPO−$SO_4^{\bullet-}$ adduct (with $a_N = 13.2$ G and $a_H = 9.6$ G) [48], which confirmed that $SO_4^{\bullet-}$ and $^{\bullet}OH$ were generated in the Fe(II)–PS and Fe(III)–PS–sulfite processes. Meanwhile, the intensity of the DMPO−$^{\bullet}OH$ adduct signals may be more obvious than that of the DMPO−$SO_4^{\bullet-}$ adduct signals in this system. This phenomenon could be explained by the partial transformation from DMPO−$SO_4^{\bullet-}$ adducts to DMPO−$^{\bullet}OH$ adducts [47,49].

To further understand the mechanism of the Fe(III)/sulfite/persulfate triple system, EtOH and TBA were selected as radical scavengers, and their effects on X-3B decolorization were measured at pH 6.0. In this experiment, EtOH and TBA were added at a 500:1 alcohol-to-oxidant molar ratio to identify the primary radical species. This method has been widely used by previous researchers, based on the fact that TBA can effectively quench agents for hydroxyl radicals, while it reacts with $SO_4^{\bullet-}$ at a negligible rate that is 1/1000 of the rate reacting with the hydroxyl radicals ($k_{\mathrm{TBA,\,HO^{\bullet}}} = (3.8\text{–}7.6) \times 10^{8}\ \mathrm{M^{-1}\ s^{-1}}$, $k_{\mathrm{TBA,\,SO_4^{\bullet-}}} = (4.0\text{–}9.1) \times 10^{5}\ \mathrm{M^{-1}\ s^{-1}}$, $k_{\mathrm{EtOH,\,HO^{\bullet}}} = (1.8\text{–}2.8) \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}}$, $k_{\mathrm{EtOH,\,SO_4^{\bullet-}}} = (1.6\text{–}6.2) \times 10^{7}\ \mathrm{M^{-1}\ s^{-1}}$) [50-52].

The data in Table 2 and Fig. A8a confirm the formation of $SO_4^{\bullet-}$ in the

Fe(III)/sulfite/persulfate triple system, which accounted for 61.1% of the decolorization of 40 mg $L^{-1}$ X-3B. $HO^{\bullet}$ was also detected in this system, which accounted for up to 28.9% of the decolorization of X-3B. Several reports have shown the relationship between $SO_4^{\bullet-}$ and $HO^{\bullet}$, and $SO_4^{\bullet-}$ can oxidize $H_2O$ or $HO^{-}$ to generate $HO^{\bullet}$ through eqs. 11 and 12 [53]. $SO_5^{\bullet-}$ and $SO_3^{\bullet-}$ can also be generated (eqs. 2, 3, 5, and 14), whereas $SO_3^{\bullet-}$ is prone to be oxidized to $SO_5^{\bullet-}$ by oxygen (eq. 3) [23]. Consequently, it infers that $SO_5^{\bullet-}$ was responsible for the decolorization of the remaining 10% of X-3B. As a control, the mechanism of the Fe(III)/sulfite system was also investigated by a quenching experiment. It was found that $SO_4^{\bullet-}$, $HO^{\bullet}$, and $SO_5^{\bullet-}$ radicals contributed to 73.9%, 16.4%, and 9.7% of the oxidation process, respectively (Fig. A8b). Therefore, $SO_4^{\bullet-}$ and $HO^{\bullet}$ were the major reactive oxygen species for the decolorization of X-3B.

### *3.6. TOC removal in the triple system*

According to the above discussion, $SO_4^{\bullet-}$ and $HO^{\bullet}$ were verified as being mainly responsible for the decolorization of X-3B. It was further expected that it may mineralize the organic contaminants in the aqueous environment. In this study, TOC removal efficiency in the Fe(III)/sulfite/persulfate triple system was evaluated, and the results are shown in Fig. 5. The TOC reduction reached only 11.4% after 12 h, but then reached 41.5%, 49.6%, and 66.4% after 18 h, 21 h, and 36 h, respectively. Merely 5% TOC removal was observed during the first 2 h in our previous work [21]. It can be considered that mineralization in the $SO_4^{\bullet-}$ generating system involves a slow reaction, which is consistent with observations by Aditya Rstogi and Wang [3,15,54]. Thus, the Fe(III)/sulfite/persulfate triple system can achieve rapid decolorization and slow mineralization of dyes. Finally, UV/vis spectra of X-3B in this system are shown in Fig. A9; the decolorization of X-3B was mainly due to the destruction of its chromophore groups (e.g., azo bonds), and this mechanism has potential for practical application in sulfite-contaminated wastewater and desulfurization of wastewater.

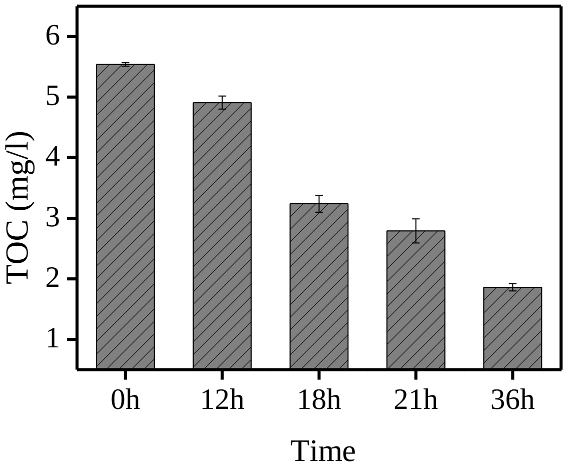


**Fig. 5** – The removal of TOC by the Fe(III)/sulfite/persulfate triple system. Reaction conditions: [X-3B] = 40 mg $L^{-1}$, $[Fe^{3+}]_0$ = 0.1mmol $L^{-1}$, $[Na_2SO_3]_0$ = 1 mmol $L^{-1}$, $[PS]_0$ = 2 mmol $L^{-1}$, pH 6.0.

### 3.7. X-3B degradation pathway

To examine the mechanism of X-3B degradation at near-neutral pH, reaction intermediates and X-3B products were identified using LC–ESI-MS. HPLC chromatograms and (+)-ESI-MS spectra of X-3B and four degradation products after 30 min reaction are presented in Fig. A10.

The proposed pathway for X-3B degradation according to the above results is illustrated in Fig. 6. Firstly, the N=N and C-N bonds are attacked by $SO_4^{\bullet-}$ or $^{\bullet}OH$, which leads to the bond breaking and a loss of small molecule fragments, such as DP 1, DP 2, DP 3 and aniline. Secondly, the fragments could be oxidized further. The chlorine atoms in DP 3 could be replaced by $^{\bullet}$OH to form DP 4 [55]. In addition, the $SO_4^{\bullet-}$ adduct wasn't observed in this work, which was different from previous work [23].

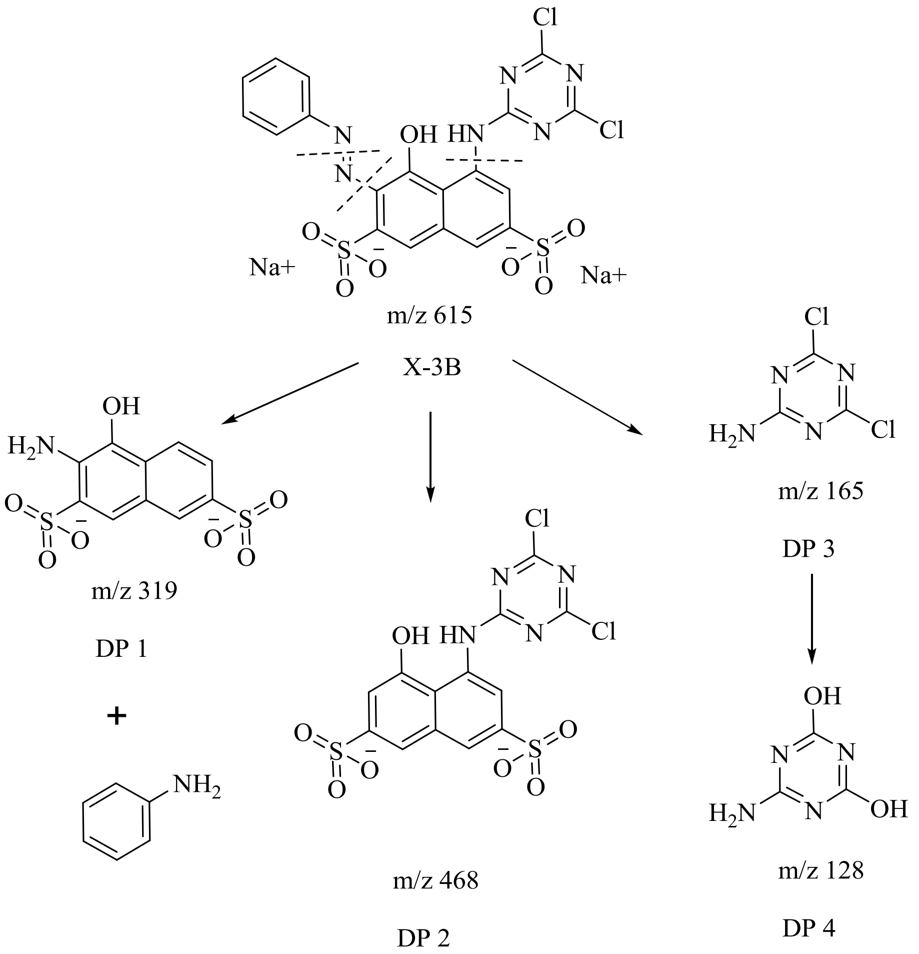


**Fig. 6** Proposed pathways for X-3B degradation in the Fe(III)/sulfite/persulfate triple system.

## 4. Conclusions

In this study, the Fe(III)/sulfite/persulfate triple system is proved be effective in rapid decolorization and partial mineralization of azo dyes. Fe(III)–sulfite complex can be used to activate persulfate and prevent Fe(III) precipitation at near-neutral pH. Approximate 85% of X-3B was decolorized within 30 min at the optimum ratio of Fe(III)/sulfite/persulfate (0.1:1:2 mmol $L^{-1}$). The decolorization efficiency of X-3B increased at lower pH and at higher concentration of oxygen presented in the solution. $SO_4^{\bullet-}$ and $HO^{\bullet}$ were identified to be the main reactive oxygen species through radical quenching and EPR/DMPO experiments, and two pathways are involved in the generation of $SO_4^{\bullet-}$ in this triple system. Furthermore, a TOC removal efficiency of 66.4% was achieved during a lengthy 36 h process due to selective oxidation by $SO_4^{\bullet-}$. The attack by the oxysulfur radicals to X-3B led to four degradation products. Therefore, this Fe(III)/sulfite/persulfate triple system can potentially be applied prospects in wastewater treatment.

## Acknowledgments

This work was supported by a grant from the National Natural Science Foundation of China (51078161, 51409108, 51508423) and Huazhong University of Science and Technology Independent Innovation Fund (0118261028). Thanks for Huazhong University of Science and Technology Analytical and Testing Center. The anonymous reviewers are also gratefully acknowledged.

## Appendix A. Supplementary information

Supplementary information associated with this article can be found in the online version.

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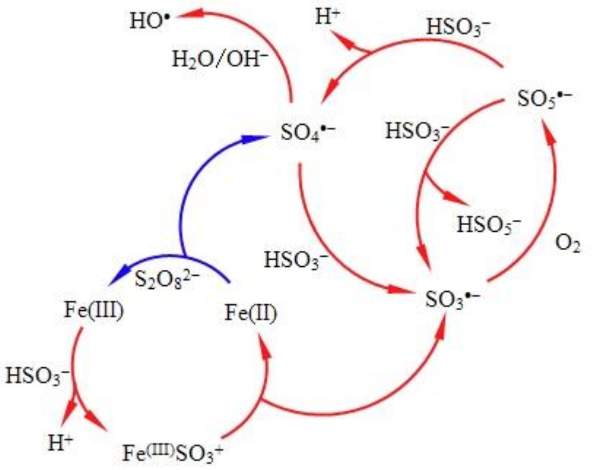
**Table 2** – Results of radical identification from the decolorization of X-3B.

| System | Decolorization of X−3B (%) | Change in decolorization of X−3B due to TBA (%) | Decolorization due to $HO^{\bullet}$ (%) | Change in decolorization of X−3B due to EtOH (%) | Decolorization due to $SO_4^{\bullet-}$ and $HO^{\bullet}$ (%) | Decolorization due to $SO_5^{\bullet-}$ (%) |
|---|---|---|---|---|---|---|
| $Fe^{3+}$/ $Na_2SO_3$/PS | 84.7 | −24.5 | 28.9 | −76.2 | 90 | 10 |
| $Fe^{3+}$/$Na_2SO_3$ | 45.2 | −7.4 | 16.4 | −40.8 | 90.3 | 9.7 |

Conditions: $[X\text{-}3B]_0 = 10$ mg $L^{-1}$, $[Fe^{3+}]_0 = 0.1$ mmol $L^{-1}$, $[Na_2SO_3]_0 = 1$ mmol $L^{-1}$, $[PS]_0 = 2$ mmol $L^{-1}$, $[TBA]_0 = [EtOH]_0 = 500$ mmol $L^{-1}$, $pH_{ini}$ 6.0



**Scheme. 1** – Pathways of $SO_4^{\bullet-}$ and ${}^{\bullet}OH$ generation in the Fe(III)/sulfite/persulfate triple system.