

# Comparative study of three solid oxidants as substitutes of H<sub>2</sub>O<sub>2</sub> used in Fe (III)-oxalate complex mediated Fenton system for photocatalytic elimination of reactive azo dye

Congcan Zhang <sup>a</sup>, Yongchun Dong <sup>a, b, \*</sup>, Bing Li <sup>c</sup>, Fu Li <sup>a</sup>

<sup>a</sup> Textile Chemistry & Ecology, School of Textiles, Tianjin Polytechnic University, Tianjin 300387, China

<sup>b</sup> Key Laboratory of Advanced Textile Composite of Ministry of Education, Tianjin Polytechnic University, Tianjin 300387, China

<sup>c</sup> Inspection and Quarantine Technology Center, Guangxi Entry-Exit Inspection and Quarantine Bureau, Nanning 530021, China

## ARTICLE INFO

### Article history:

Received 23 March 2017

Received in revised form

17 December 2017

Accepted 24 December 2017

Available online 28 December 2017

### Keywords:

Solid oxidants

Fe (III) ions

Oxalate

Dye degradation

Reactive oxygen species

## ABSTRACT

Degradation of an azo dye, Reactive Red 195 was conducted with four oxidants including H<sub>2</sub>O<sub>2</sub>, sodium percarbonate (SPC), sodium perborate (SPB) and sodium persulfate (SPS) in the presence of Fe (III)-oxalate complex under light irradiation to investigate the feasibility of three solid oxidants as substitutes of H<sub>2</sub>O<sub>2</sub> for building a novel solar light-driven Fenton system with the advantages of high stability, cost efficiency and environmental care. Some important effecting factors such as initial concentrations of Fe (III) ion, oxalate ion and oxidant, temperature and light irradiation were also examined and optimized with respect to dye degradation efficiency. The results indicates that dye could be completely degraded using each solid oxidant in place of H<sub>2</sub>O<sub>2</sub> over 30 min with Fe (III)-oxalate complex under visible irradiation. SPC showed higher oxidizing performance compared with the other two solid oxidants, especially at higher temperature or in the presence of inorganic salt. Hydroxyl radicals (\*OH) was identified as the predominant reactive oxygen species for three solid oxidants, especially SPC. Sulfate radicals (\*SO<sub>4</sub><sup>-</sup>) were found for SPS system. However, it has a less contribution to dye degradation than \*OH. Besides, superoxide radicals (O<sub>2</sub><sup>-</sup>) also participated in dye degradation in all investigated systems.

© 2017 Published by Elsevier Ltd.

## 1. Introduction

Fe (III)-oxalate complex mediated oxidation system is generally more efficient than the simple Fenton system for controlling industrial wastewater pollution because of two main advantages: one is that Fe (III)-oxalate complex accelerate the generation of Fe(II) ions and a series of reactive oxygen species (ROS) through absorbing solar light (Liu et al., 2010; Vedrenne et al., 2012; Zhao et al., 2014), and the other is that this system is capable of degrading a variety of organic pollutants at near neutral pH due to the presence of suitable ligands (Ayodele et al., 2012; Bautitz and Nogueira, 2010; Katsumata et al., 2010). Besides, oxalate can react with dissolved oxygen in water to form superoxide radicals (O<sub>2</sub><sup>-</sup>) that are likely to produce H<sub>2</sub>O<sub>2</sub> (Vedrenne et al., 2012). In the last

several decades, Fe (III)-oxalate complex based Fenton process as a popular in-situ chemical oxidation (ISCO) has been used in the removal of organic contaminants from water and wastewater systems. It is well known that H<sub>2</sub>O<sub>2</sub> is the most commonly used oxidizing agent in this Fenton process for degrading a number of organic compounds such as dyes, surfactants and phenols etc (Ayodele et al., 2012; Bautitz and Nogueira, 2010; Dong et al., 2008a, 2007; Katsumata et al., 2010; Liu et al., 2010; Vedrenne et al., 2012; Zhao et al., 2014). because it is a cheap and environmentally friendly oxidant (Habibi et al., 2009). This process is based on the sunlight-enhanced generation of the highly reactive hydroxyl radicals (\*OH), which oxidize the organic pollutants in water and convert it completely into water, carbon dioxide and inorganic compounds (Dong et al., 2008b, 2007). However, it is a fact that the handling of concentrated H<sub>2</sub>O<sub>2</sub> solutions is not desirable for safety problems, and H<sub>2</sub>O<sub>2</sub> rarely has a half-life more than 48 h (Habibi et al., 2009; Wu et al., 2014). Therefore, an attempt should be made to find alternative oxidizing agents with higher stability and similar activity instead of H<sub>2</sub>O<sub>2</sub> for the Fe (III)-oxalate complex based Fenton process. The survey of the recent literature revealed

\* Corresponding author. Division of Textile Chemistry & Ecology, School of Textiles Tianjin Polytechnic University, 399 Binshui West Road, Xiqing District, Tianjin 300387, China.

E-mail addresses: [teamdong@sina.cn](mailto:teamdong@sina.cn), [dye@tjpu.edu.cn](mailto:dye@tjpu.edu.cn) (Y. Dong).

that several solid oxidizing agents, especially persulfate (Gao et al., 2016; Lee et al., 2015; Matzek and Carter, 2016; Wu et al., 2014; Xie et al., 2015), percarbonate (Fu et al., 2015; Habibi et al., 2009; Miao et al., 2015a, 2015b; Zang et al., 2014) and perborate (Habibi et al., 2009) were extensively applied for different types of ISCO technologies due to their advantages of cost effectiveness, high activity and the environmentally friendly nature. Additionally, they are relatively stable solids and are thus easy to handle on a large-scale and permit accurate dosage (Habibi et al., 2009). Specifically, sodium persulfate (SPS) has been found to be activated by heat, light irradiation or transition metal ions to produce free sulfate radicals ( $\bullet\text{SO}_4^-$ ) with a high oxidation potential ( $E^0 = 2.6\text{ V}$ ), which is comparable to that of  $\bullet\text{OH}$  ( $E^0 = 2.7\text{ V}$ ) (Wu et al., 2014). Furthermore,  $\bullet\text{SO}_4^-$  is more efficient than  $\bullet\text{OH}$  to oxidize some refractory organic compounds due to its selective oxidation ability (Wu et al., 2014). Sodium perborate (SPB) and sodium percarbonate (SPC) are considered as versatile oxidizing agents in a wide pH range because they are nontoxic solids with exceptional storage stability and no shock sensitivity, which have been extensively used for oxidation of different types of functional groups in organic chemistry (Habibi et al., 2009; Zhu et al., 2008). SPC and SPB act as sources of  $\text{H}_2\text{O}_2$ , if dissolved in water. Their properties in aqueous solution are practically similar to those of a  $\text{H}_2\text{O}_2$  solution (Miao et al., 2015a, 2015b). In comparison with SPB, SPC can generate more oxygen and offer higher solubility at room temperature, and does not introduce any additional potentially harmful by-products into the water matrix (Miao et al., 2015a). Hence, this work aims at the comparative evaluation of SPS, SPC, SPB and  $\text{H}_2\text{O}_2$  as the oxidizing agents for the degradation of a typical azo dye, Reactive Red 195 in Fe (III)-oxalate complex based Fenton process. Feasibility of three solid oxidizing agents used for this process was investigated through determining efficiency of Fenton oxidation of the dye using each solid oxidizing agent in various conditions. Besides, their oxidation mechanisms were discussed and proposed.

## 2. Experimental

### 2.1. Reagents and chemicals

Analytical grade hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30%), ferric sulfate ( $\text{Fe}_2(\text{SO}_4)_3$ , >99.0%), oxalic acid (OA,  $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , >99.0%), sodium percarbonate (SPC,  $\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2$ , >98%), sodium perborate tetrahydrate (SPB,  $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ , >98%), sodium persulfate (SPS,  $\text{Na}_2\text{S}_2\text{O}_8$ , >99%), isopropyl alcohol (IPA,  $(\text{CH}_3)_2\text{CHOH}$ , >99.5%), tert-butyl alcohol (TBA,  $(\text{CH}_3)_3\text{OH}$ , >99.0%) and 1, 4-benzoquinone (BQ,  $\text{C}_6\text{H}_4\text{O}_2$ , >97%) were used without further purification. 5,5-dimethyl-1-pyrroline-N-oxide (DMPO, >97%) was purchased from Micklin Biochemical Technology Co., Ltd (Shanghai, China). A typical commercial azo dye, Reactive Red 195 (RR 195, CAS: 93050-79-4) was used after purification by the re-precipitation method

(Greaves et al., 2001). Its molecular structure is presented in Scheme 1. This dye was selected as the model dye in this work mainly because of its high consumption rate in China for dyeing cotton and rayon textiles. All solutions were prepared in deionized water.

### 2.2. Experimental procedures

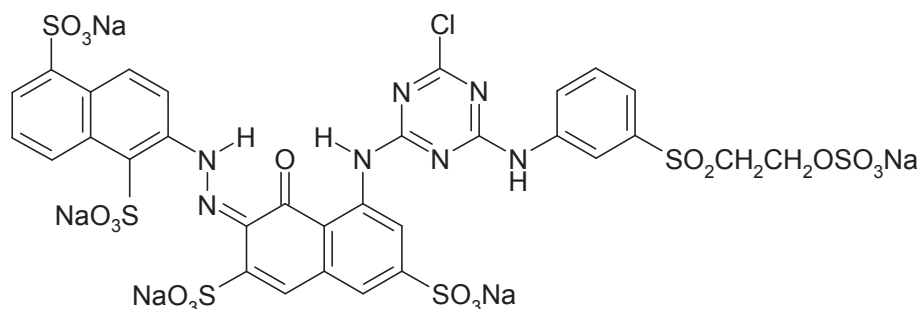
All dye degradation experiments were carried out in a specially designed photoreaction reactor composed mainly of chamber, electromagnetic valve, relay, water bath, and high pressure mercury lamp (400 W, Osram Foshan Illuminance Co., China) or 365 nm UV lamp (150 W, Shanghai Philips-Yamin Co., China). Its schematic diagram was presented in our previous study (Han et al., 2011). A cut-off filter was used to ensure irradiation only by visible light ( $\lambda > 420\text{ nm}$ ) for high pressure mercury lamp. The visible or UV light intensity over the test solution surface was measured using an FZ-A radiometer or UV-A radiometer (Beijing BNU Light and Electronic Instrumental Co., China). Test solutions containing RR 195 ( $0.05\text{ mmolL}^{-1}$ ), OA,  $\text{Fe}_2(\text{SO}_4)_3$ , oxidant ( $\text{H}_2\text{O}_2$ , SPS, SPC or SPB) were made and then placed into reaction beakers in the photoreaction reactor. Their initial pH level was adjusted to be 6.0 with dilute NaOH or  $\text{H}_2\text{SO}_4$  aqueous solution, and determined by using DHS-25C digital pH meter (Shanghai Jingmi Instrumental Co., China). Dye degradation reaction was started by adding given oxidant dosage and time calculated. To investigate the free oxygen radicals generated during reaction and their contribution to dye degradation, three radical scavengers IPA ( $\bullet\text{OH}$  and  $\bullet\text{SO}_4^-$  scavenger), TBA ( $\bullet\text{OH}$  scavenger, but not  $\bullet\text{SO}_4^-$ ) (Buxton et al., 1988; Monteagudo et al., 2011) and BQ ( $\text{O}_2\bullet$  scavenger) (Buxton et al., 1988; Wu et al., 2014) were selected and adopted in the dye degradation experiments according to their reactive activities with each of the free oxygen species potentially present in Fe (III)-OA complex/oxidant systems. All the experiments were carried out in triplicate. The results were expressed as the mean value. Standard deviation is less than 5.0% of the mean value.

### 2.3. Analytical methods

The concentration of RR 195 in test solution during the experiment was determined using a UV-2401 spectrophotometer (Shimadzu Co., Japan) at the maximum absorption wavelength ( $\lambda_{\text{max}} = 522\text{ nm}$ ). Dye decoloration percentage at a given time was calculated as:

$$D\% = (1 - C_t/C_0) \times 100\% \quad (1)$$

where  $C_0$  was the initial concentration of the dye ( $0.05\text{ mmolL}^{-1}$ ), and  $C_t$  was the concentrations of the dye in test solution at a given time ( $\text{mmolL}^{-1}$ ). The content of total organic carbon (TOC) of test



Scheme 1.

Download English Version:

<https://daneshyari.com/en/article/8098660>

Download Persian Version:

<https://daneshyari.com/article/8098660>

[Daneshyari.com](https://daneshyari.com)