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Research article

# Effect of chelating agents on Reactive Green 19 decolorization through $Fe^0$-activated persulfate oxidation process

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ABSTRACT

The effect of chelating agents on the decolorization of Reactive Green 19 (RG19) through $Fe^0$ activated persulfate ($PS/Fe^0$) process was investigated. Though other previous studies reported that chelating agent can enhance the degradation of organic contaminant in Fenton-like system, our finding showed that the presence of chelating agents would chelate free $Fe^{2+}$ and minimize free $Fe^{2+}$ concentration, which resulted in the retardation of RG19 decolorization. RG19 decolorization decreased to 7%, 21%, and 15% in the presence of sodium citrate, sodium EDTA, and sodium oxalate, compared with control test (without chelating agent, 99%) within 10 min. The degradation efficiencies decreased with increasing chelating agent concentrations because of complex formation with $Fe^{2+}$. Higher PS concentration, $Fe^0$ dosage, and temperature had an obvious enhancement for RG19 decolorization efficiency. Elucidation of RG19 containing sodium EDTA degradation pathways indicated that $PS/Fe^0$ process could degrade RG19 to carboxylic acids and inorganic salts efficiently. The presence of sodium EDTA had no influence on by-products, and EDTA just played a chelating agent function for chelating Fe ions.



## 1. Introduction

Azo dyes are an abundant class of pure synthetic organic compounds, which are characterized by the presence of one or more azo-bonds. Generally, over 15% of the textile dyes are lost in wastewater stream during the synthesis and dyeing processes (Dong et al., 2008), which can cause environmental problems (Jorfi et al., 2017; Liu et al., 2017). Discharge of colored effluents to water limits the sun light penetration and vision, and therefore interferes the algal and aquatic plants photosynthesis (Jorfi et al., 2016). Usage of untreated dyeing effluents for the agriculture purpose has direct impact on the fertility of soil (Kalyani et al., 2009). In addition, Lade et al. (2012) reported that the presence of the dye Rubine GFL (1000 ppm) would have an inhibition of germination for *Sorghum vulgare* and *Phaseolus mungo*. Therefore, much attention has been paid for the removal of azo dyes.

Persulfate (PS) oxidation process is one of the most promising methods for the elimination of toxic and bio-resistant organic compounds (Hilles et al., 2016; Ko et al., 2012; Liu et al., 2016; Sharma et al., 2015; Weng and Tsai, 2016). Various catalysts have been used to catalyze PS in the past decades, such as $Fe^0$ (Li et al., 2017b; Zeng et al., 2017), $Fe^{2+}$ (Ge et al., 2016), zero valent copper (Ghanbari et al., 2014), and activated carbon (Yang et al., 2011). All these materials show high efficiency in activating PS to produce $SO_4^{\bullet-}$. $Fe^0$ activated PS process is frequently considered as a heterogeneous reaction for removing organic compounds (Li et al., 2017a; Wang et al., 2014; Weng et al., 2015; Zou et al., 2014), which offers some advantages over the classical transition metals/persulfate homogeneous reaction, including low cost, operation at a wide pH range, and the possibility to recycle the iron.

Chelating agents have been used in various industrial processes including metal finishing, textile manufacturing, and paper-pulp production (Liang et al., 2009). They were used to moderate the negative influence of transition metal ions on the industrial process. The presence of chelating agents in dyeing effluents can chelate with the free ferrous or ferric ions, which can affect the decolorization of dyeing wastewater by Fenton or Fenton-like treatment (Dong et al., 2007, 2008; Niu et al., 2012).

Previous studies have shown the influence of chelating agents on Fenton or Fenton-like processes (Dong et al., 2008; Peng et al., 2015; Xu et al., 2014). Niu et al. (2012) demonstrate Fe(II)-EDTA catalyzed persulfate could effectively enhance the degradation of Orange G in a microbial fuel cell compared with Fe(II)/persulfate (EDTA 0.0 mmol/L) system. Guo et al. (2011) report the photo-

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degradation of methyl orange was greatly enhanced in the presence of Fe(III) and citrate acid compared with Fe(III) or citrate acid alone. The presence of oxalate promoted the Fenton oxidation of microcystin-LR using nanoscale zero-valent iron (nZVI) as the catalyst, and oxalate stimulated the production of hydroxyl radicals (Wang et al., 2016). Xue et al. (2009) investigate the effect of six chelating agents on the oxidation rate of pentachlorophenol (PCP) by magnetite activated $H_2O_2$ system. They found the presence of chelating agents improved the PCP oxidation rate, and EDTA-driven Fenton reaction showed the highest oxidation rate among six chelating agents.

Current studies focus on the influence of chelating agents on the degradation of the organic compounds by Fenton or Fenton-like processes, using iron oxides, nZVI, or ferrous or ferric ions as catalysts. However, very limited information is available on the decomposition of diazo dyes containing chelating agents, especially using $Fe^0$ activated persulfate process (PS/$Fe^0$). Furthermore, the influence of chelating agents on degradation of organic contaminant by PS/$Fe^0$ process was also not reported.

In this study, the influence of chelating agents on the decomposition of diazo dye RG19 through PS/$Fe^0$ process was studied. Three chelating agents, sodium citrate, sodium EDTA, and sodium oxalate, were selected, which were widely used in industrial processes among a variety of chelating agents. Moreover, the degradation of RG19 was examined under different conditions (chelating agent concentration, dosage of $Fe^0$ and persulfate, and temperature). The UV–visible spectra, chemical oxygen demand (COD), and the possible degradation pathways of RG19 were also investigated.

## 2. Materials and methods

### 2.1. Materials

Reactive Green 19 (RG19, $C_{40}H_{23}Cl_2N_{15}Na_6O_{19}S_6$, CAS No. 61931-49-5) (Fig. 1) was obtained from Sigma (China). $Fe^0$ aggregates were obtained from Connelly-GPM Inc. (USA) with particle size 0.297–2.380 mm and specific weight 2240–2560 kg/$m^3$. Sodium persulfate ($Na_2S_2O_8$) was purchased from Sinopharm Chemical Reagent CO., Ltd (China). Sodium citrate, sodium EDTA, and sodium oxalate were purchased from Sinopharm Chemical Reagent CO., Ltd (China). All other reagents were in analytical grade.

### 2.2. Persulfate oxidation procedure

Experiments were conducted at ambient temperature (25 ± 2 °C), except stated, fresh dye solutions were mixed with $1 \times 10^{-3}$ M sodium citrate, sodium EDTA, and sodium oxalate, respectively. Unless otherwise stated, the experimental procedures were as follows: (1) the solution pH was adjusted to a predetermined value using 0.01 M HCl/NaOH. (2) 1.0 g/L $Fe^0$ aggregates and $5 \times 10^{-3}$ M PS were added to solution at the start of the experiment. (3) The solution was immediately agitated with a mechanical stirrer (Shin-Kwang, Taiwan) at 800 rpm for 30 min. (4) 10 mL of solution was taken from the reactor at predetermined time and filtered immediately through a 0.45-μm membrane filter (Tianjin Jinteng Experiment Equipment Co., Ltd, China) (5) The residual RG19 concentration and American Dye Manufactures Institute (ADMI) value in the filtrates were determined.

The effect of chelating agent concentration on RG19 decolorization was conducted by mixing 1000 mL fresh dye solution with chelating agents (sodium citrate, sodium EDTA, and sodium oxalate, respectively) in concentration as 0, $5 \times 10^{-4}$, $1 \times 10^{-3}$, $2 \times 10^{-3}$, $5 \times 10^{-3}$, and $1 \times 10^{-2}$ M. The effect of $Fe^0$ dosage and PS concentration was also investigated under0.1, 0.25, 0.5, 1.0, 1.5, 2.0 g/L $Fe^0$ dosages and $5 \times 10^{-4}$, $1 \times 10^{-3}$, $2 \times 10^{-3}$, $5 \times 10^{-3}$, $1 \times 10^{-2}$, $2 \times 10^{-2}$ M PS concentrations.

The effect of temperature on PS/$Fe^0$ process decolorization was investigated under the initial temperature conditions at 10, 25, 40, and 55 °C using an electric stove, and the other operating parameters were RG19 $5 \times 10^{-5}$ M, $Fe^0$ 1.0 g/L, PS $5 \times 10^{-3}$ M, chelating agent $1 \times 10^{-3}$ M, and initial pH 6.0.

The concentration of free ferrous ions and total Fe was measured as the followed steps: (1) the standard curves of free ferrous ions (and total Fe) was made by using the standard solution of ferrous ion (and Fe) and Hach Ferrous ions reagent (and FerroVer® iron reagent, Hach Co., Loveland, USA). (2) two sample solution of 10 mL was taken from the reactor at predetermined time and filtered immediately through a 0.45-μm membrance filter. (3) 15 mL ethyl alcohol as $SO_4^{-\bullet}$ scavengers was added into each sample solutions. (4) a pack of Ferrous Ion reagent (and FerroVer® iron reagent) was added into one sample solution and blended well, the other sample solution as the blank control. (5) after 3 min, the concentration of $Fe^{2+}$ (and total Fe) in the filtrates was analyzed. Each decolorization experiment was conducted in duplicate, and mean values were reported.

### 2.3. Analytical methods

The RG19 was analyzed using a spectrophotometer (Hach DR/3900, USA) at 626 nm. The concentration of $Fe^{2+}$ in solution was analyzed at 510 nm. Chemical oxygen demand (COD) was determined by Hach Method 8000 reactor digestion method with the Hach spectrophotometer. This method was USEPA approved for wastewater analyses (Standard Method 5220D) (APHA et al., 2012).

Because residual PS ([PS] in mol/L) in the solution affected COD (mg/L) measurements, a real COD was empirically calculated using the relationship between measured COD and interference of PS (Weng et al., 2015). Residual PS concentration was spectrometrically determined using ferrous ammonium sulfate (FAS) method (Huang et al., 2002). At various time intervals, 0.1 mL of reaction solution was placed in a 20 mL test tube and 0.9 mL of distilled water, 10 mL of 2.5 M $H_2SO_4$ solution and 0.1 mL of 0.4 M FAS solution were added. The solution was mixed and reacted for 40 min. Upon completion, 0.2 mL of 0.6 M $NH_4SCN$ solution was added. Finally, the absorbance was measured using the spectrophotometer at 450 nm.

The potential intermediate products of RG19 were identified using GC-MS (Agilent 6890A/5973C) equipped with a capillary

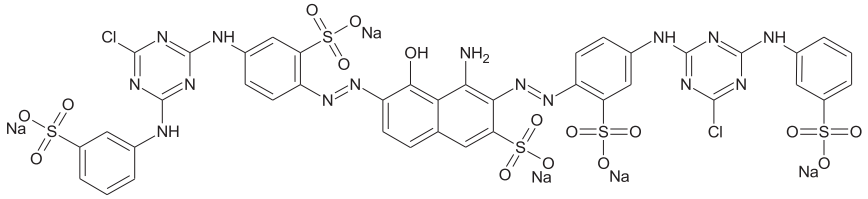

**Fig. 1.** The structural formula of Reactive Green 19.