



## Research article

# Effective degradation of primary color direct azo dyes using Fe<sup>0</sup> aggregates-activated persulfate process



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## ABSTRACT

The present study examined the oxidation power of a Fe<sup>0</sup> aggregates/persulfate (PS/Fe<sup>0</sup>) system for the degradation of the wastewater containing mixed primary direct dyes (i.e., Sirius<sup>®</sup> Gelb S-2G, Sirius<sup>®</sup> Red F3B, and Sirius<sup>®</sup> Turkis GL01). Results indicated that decolorization efficiency was determined by operating parameters of the PS/Fe<sup>0</sup> system and the structural complexity of dye molecules. System efficiency increased with increasing persulfate and Fe<sup>0</sup> dosages. Faster decolorization was observed in experiments conducted at pH < 10. The process obeyed a first-order kinetics. Slow heterogeneous reactions were observed at high initial pH (>10.5) and low PS concentration (<2 × 10<sup>-3</sup> M). Inhibitory effect occurred in systems containing salts Na<sub>2</sub>SO<sub>4</sub>, NaCl, Na<sub>2</sub>CO<sub>3</sub>, and Na<sub>2</sub>HPO<sub>4</sub> at 1 × 10<sup>-2</sup> M. The effect was suppressed when reaction temperature was raised to 55 °C. Heat enhanced not only decolorization efficiency, but also COD removal. Complete decolorization of a mixed dye containing ADMI (the American Dye Manufacture Institute) 15105 was achieved within 10 min in the PS/Fe<sup>0</sup>/55 °C system with an initial pH of 6.0 and dosages of 5 × 10<sup>-3</sup> M Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and 0.5 g/L Fe<sup>0</sup>. Low molecular weight intermediates including organic acids were identified. Due to a relatively low activation energy (4.68 kcal/mol), the PS/Fe<sup>0</sup> system exhibited higher efficiency at higher temperature. This study demonstrated that Fe<sup>0</sup>-activated PS is a promising process for the treatment of textile wastewaters containing mixed azo direct dyes.

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## 1. Introduction

Textile and dyeing wastewaters contain synthetic dyes which give strong color that can be aesthetically undesirable even at relatively low concentrations. The molecules of azo dyes contain an azo bond (–N=N–) associated with benzene or naphthalene which is highly resistant to natural degradation. Azo dyes can also be toxic to aquatic life (Ferraz et al., 2011). Conventional activated sludge processes are usually inadequate for the treatment of azo dyes under the increasingly stringent effluent standards. Azo-dyes are stable and highly resistant to microbial degradation due to their complex molecular structures. However, many of these dyes can be readily destructed by strong oxidizing radicals such as sulfate radical (SO<sub>4</sub><sup>•-</sup>) and hydroxyl radical (HO<sup>•</sup>) in Advanced Oxidation Processes (AOPs) (Ferkous et al., 2017; Liu et al., 2016; Shang et al.,

2017; Weng et al., 2013a; Weng and Tsai, 2016).

With oxidation potentials (E<sup>0</sup>) up to 2.60 and 2.72 electron volts (V) respectively, sulfate and hydroxyl radicals are highly reactive (Buxton et al., 1988). They are capable of non-selectively oxidizing various forms of organic contaminants. SO<sub>4</sub><sup>•-</sup> radicals have a much longer lifetime than HO<sup>•</sup> radicals (30–40 μs versus 0.02 μs) (Pikaev and Zolotarevskii, 1967). SO<sub>4</sub><sup>•-</sup> radicals are reactive within a wide range of pH while HO<sup>•</sup> radicals are reactive only at pH < 3.5. SO<sub>4</sub><sup>•-</sup> radicals also have higher standard redox potentials in the abduction of electrons (2.5–3.1 V versus 1.89–2.71 V) (Buxton et al., 1988; Neta et al., 1988). SO<sub>4</sub><sup>•-</sup> radicals are relatively stable at room temperature. Due to their selectivity, SO<sub>4</sub><sup>•-</sup> radicals are more potent than HO<sup>•</sup> radicals in oxidizing recalcitrant organic compounds containing aromatic constituents and unsaturated bonds (Neta et al., 1988).

SO<sub>4</sub><sup>•-</sup> radicals can be generated from the activation of persulfate (PS) and peroxymonosulfate (PMS) via electron transfer with transition metals (Me<sup>n+</sup>) such as Ag, Co, Cu, Fe, Mn, V, and Fe (Fang et al., 2017; Li et al., 2017a,b; Liu et al., 2016; Ma et al., 2017). Base

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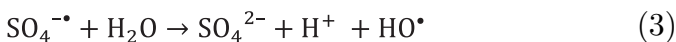
can also be used to activate persulfate (Furman et al., 2010). Two  $\text{SO}_4^{\bullet-}$  radicals can be produced from a persulfate anion via the input of heat, ultraviolet light, microwave, or ultrasound (US). The processes impart energy to the persulfate anion causing cleavage of the peroxide bond (Eq. (1)) (Ferkous et al., 2017; Gao et al., 2017; Matzek and Carter, 2016).



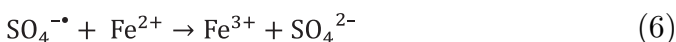
A  $\text{SO}_4^{\bullet-}$  radical can be formed from the reduction of a persulfate anion by a transition metal donating one electron through the radiolysis of water (Eq. (2)) (Anipsitakis and Dionysiou, 2004).



The occurrence of  $\text{SO}_4^{\bullet-}$  and  $\text{HO}^{\bullet}$  radicals are highly sensitive to solution pH. In an acidic environment,  $\text{SO}_4^{\bullet-}$  radicals are the primary oxidant involved.  $\text{HO}^{\bullet}$  radicals can be generated in all ranges of pH via the hydrolysis of  $\text{SO}_4^{\bullet-}$  radicals (Eq. (3)). These groups represent the two dominant oxidative species under alkaline conditions (Eq. (4)) (Liang and Su, 2009).



Fe is the most studied activator for the persulfate process due mainly to its low cost and environmental friendliness. Although ferrous salts are capable of delivering  $\text{Fe}^{2+}$  ions for direct activation of PS in solutions, a well-controlled supply of the ions is necessary. A second-order rate constant for the generation of  $\text{SO}_4^{\bullet-}$  radicals in a  $\text{Fe}^{2+}$ -activated persulfate process (Eq. (5)) is  $2 \times 10^{-1}$  L/mol-sec at 22 °C (Liang et al., 2008) while a second-order rate constant for the scavenging of  $\text{SO}_4^{\bullet-}$  by  $\text{Fe}^{2+}$  ions (Eq. (6)) is  $4.6 \times 10^9$  L/mol-sec (Buxton et al., 1988). The rate constants clearly show that  $\text{SO}_4^{\bullet-}$  radicals are scavenged much faster than its formation when excessive  $\text{Fe}^{2+}$  ions are available. Therefore, although oxidation power of the process can suffer from insufficient supply of  $\text{Fe}^{2+}$  ions, an over-dose can also render the system inefficient (Li et al., 2014; Vicente et al., 2011).

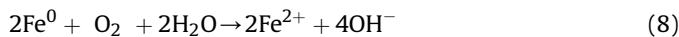


A growing attention has been given to studies on the indirect activation of PS by zero-valent iron ( $\text{Fe}^0$ ) for the degradation of azo dyes (Li et al., 2014; Raman and Kanmani, 2016; Rodriguez et al., 2014; Wang et al., 2014; Weng et al., 2015; Weng and Tsai, 2016) and recalcitrant organic contaminants such as 4-chloro-3-methyl phenol (Xu and Wang, 2011), antibiotic sulfadiazine (Zou et al., 2014), *p*-chloroaniline (Hussain et al., 2012), *p*-nitrophenol (Li et al., 2017a), 2,4-dichlorophenol (Li et al., 2017b), ciprofloxacin (Matzek and Carter, 2017), and other priority and emerging pollutants (Rodriguez et al., 2017). In a  $\text{Fe}^0$ -activated persulfate system,  $\text{Fe}^0$  induces indirect activation of persulfate via the pathway of Eq. (7). The  $\text{Fe}^{2+}$  ions generated then follow the direct activation formula of Eq. (5).



More  $\text{Fe}^{2+}$  ions are released through reactions shown in Eqs. (8)

and (9) under acidic conditions:



The release of  $\text{Fe}^{2+}$  ions from Eqs. (7) and (9) is much faster than that from Eq. (8), particularly when micro-sized and nano-sized  $\text{Fe}^0$  (Xu and Wang, 2011) are used as activators. Additionally, the reduction of  $\text{Fe}^{3+}$  ions by  $\text{Fe}^0$  also generates  $\text{Fe}^{2+}$  (Eq. (10)).



The production of  $\text{Fe}^{2+}$  ions enables a continuous generation of  $\text{SO}_4^{\bullet-}$  radicals from  $\text{Fe}^0$ -activated persulfate. Although efficient, the high costs and difficulties in handling have prevented nano-sized  $\text{Fe}^0$  from practical application in AOPs (Liu et al., 2016). Besides, the optimization of  $\text{Fe}^0$  dosage in a persulfate system using nano-sized  $\text{Fe}^0$  is difficult due to a rapid reaction and the highly variable contaminant concentration (Weng and Tsai, 2016).  $\text{Fe}^0$  aggregates have long been used commercially as a reducing agent, particularly in the remediation of groundwater. The price of  $\text{Fe}^0$  aggregates is much lower than the nano-sized  $\text{Fe}^0$  (500 USD/ton versus 80 USD/kg).  $\text{Fe}^0$  aggregates are also easier to handle and apply than the micro-sized  $\text{Fe}^0$  powders since the aggregates are relatively stable, easily separable, and reusable.  $\text{Fe}^0$  aggregates have been successfully applied in the activation of persulfate for dye degradation (Liu et al., 2016; Weng and Tsai, 2016). However, in all cases, a single dye was targeted. Since textile wastewater usually contains a variety of chemical dyes, the efficiency of such a process is uncertain when treating real wastewaters. Therefore, studies using a mixture of primary dyes are necessary for the evaluation of such a process in treating real wastewaters.

Red, yellow and blue (RBY) are the three primary colors that make up all hues. Sirius® Gelb S-2G (SGS2G), Sirius® Red F3B (SRF3B), and Sirius® Turkis GL01 (STGL01) make up as one set of color triad. They are the commonly used dyes for coloring cellulose-based fibers, therefore were selected as the target dyes in this study. Studies on the treatment of wastewaters containing a mixture of these dyes are currently unavailable in literature. In this study, commercialized  $\text{Fe}^0$  aggregates were used in the  $\text{Fe}^0$  activated PS oxidation (PS/ $\text{Fe}^0$ ) of individual primary dyes and a mixture of these dyes. Because colored industrial effluents are highly erratic in both hues and intensity of color, the concentration of dyeing agent cannot be used as an indicator of color intensity. Instead, the true color indicator of the American Dye Manufacture Institute (ADMI) is commonly adopted. The ADMI color value provides an objective measurement of color in water independent of the hue. The primary objective of this study was to compare the efficiency of various PS/ $\text{Fe}^0$  processes for the decolorization of solutions containing primary dyes, individually and as a mixture. Critical parameters including  $\text{Fe}^0$  dosage, PS concentration, reaction temperature, pH, and interferences from inorganic salts, were also determined. Intermediates from the break-up of dye molecules were also identified. Findings from this study can be valuable in the application of  $\text{Fe}^0$  activated persulfate process for the treatment of dye laden wastewaters.

## 2. Materials and methods

### 2.1. Materials

Synthetic primary dyes, namely Sirius® Gelb S-2G (SGS2G), Sirius® Red F3B (SRF3B), and Sirius® Turkis GL01 (STGL01) were obtained from DyStar (Germany). Molecular formula and

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