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## Research article

## Sulfate radical induced degradation of Methyl Violet azo dye with CuFe layered doubled hydroxide as heterogeneous photoactivator of persulfate

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## ABSTRACT

Persulfate (PS)-based advanced oxidation processes have aroused considerable attentions due to their higher efficiency and wider adaptability to the degradation of bio-recalcitrant organic contaminants. In this study, Cu-Fe layered doubled hydroxide (CuFe-LDH) was employed to degrade Methyl Violet (MV) through heterogeneous photo-activation of PS under visible-light irradiation. The reaction kinetics, degradation mechanism, catalyst stability were investigated in detail. Under the conditions of CuFe-LDH (3:1) dosage 0.2 g/L, PS concentration 0.2 g/L and without initial pH adjustment, 20 mg/L MV was almost completely degraded within 18 min. Electron Spin Resonance (ESR) test and radical quenching experiment indicated that sulfate radicals ( $\text{SO}_4^{\cdot-}$ ) were the dominant reactive oxidants for the MV decolorization, while hydroxyl radicals ( $\cdot\text{OH}$ ) were also involved. The CuFe-LDH/PS/Vis system was applicable at wide range of pH level (3–9). However, extreme pH level would lead to the reduction or transformation of  $\text{SO}_4^{\cdot-}$ . The catalyst CuFe-LDH exhibited excellent stability and maintained relatively high catalytic activity to PS even after four recycles. Mechanism study revealed that the redox cycle of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and  $\text{Cu}^{2+}/\text{Cu}^{3+}$  assisted by visible-light irradiation accounted for the enhanced generation of radicals in CuFe-LDH/PS/Vis system, resulting in the improved degradation of organic contaminants. Overall, the CuFe-LDH/PS/Vis process could be a promising approach for the removal of refractory organic pollutants in wastewater.

## 1. Introduction

Over past decades, organic dyes have been widely used in numerous industries, such as textile, paper, cosmetics, photoelectrochemical cells and so on (Shamsipur and Rajabi, 2014). According to the statistics, the average discharge of dye materials from the industrial sectors is 30,000–150,000 tons annually in the world (Das et al., 2018). Organic dyes usually have toxic, recalcitrant and/or non-biodegradable characteristics (Dhanalakshmi et al., 2016). About 15% of dyes might be released into waters from the dyeing process, undoubtedly, it would pose potential threats to ecosystems even directly to human beings. The previous studies have revealed that excessive and long-term introduction of dyes would cause serious risks to microorganisms and mammalian cells (Collazzo et al., 2012). As a consequence, it is of great necessity to construct an effective method for the elimination of pestilent dyes in the polluted waters.

Adsorption, chemical oxidation and biological degradation were feasible to remove organic pollutants including organic dyes from wastewater (Moreira et al., 2013; Chen et al., 2017a). Nevertheless, it should be noticed that adverse effects can be aroused in the adsorption and flocculation processes, for example, massive solid waste production and possible secondary pollution (Gong et al., 2017). Biodegradation often requires a comparatively long time and sophisticated facilities (Lin and Zhang, 2017). Recently, advanced oxidation process (AOP), a novel chemical oxidation process, has been regarded as one of effective, environmentally-friendly and relatively low cost methods for the dye-containing wastewaters treatment (Mousavi et al., 2018; Pirhashemi et al., 2018). Among them, hydroxyl ( $\cdot\text{OH}$ ) (Akhundi and Habibi-Yangjeh, 2017) or sulfate radical ( $\text{SO}_4^{\cdot-}$ )-based AOPs have been widely used in the degradation of dye, pesticide, antibiotic, pharmaceutical residual and so on. However, the application of  $\cdot\text{OH}$ -involved AOPs, such as UV/ $\text{H}_2\text{O}_2$ , Fenton and photo-Fenton are more or less

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constrained by their shortcomings: relatively fussy operation, tedious synthetic steps, the limited pH range, and rapid decay of the catalyst in the effluent (Chai et al., 2016; Jia et al., 2016). Compared with  $\cdot\text{OH}$  ( $E_0 = 1.8\text{--}2.7\text{ V}$ ),  $\text{SO}_4^{\cdot-}$  has a comparable standard redox potential ( $E_0 = 2.5\text{--}3.1\text{ V}$ ), a longer lifetime (4s) and wider pH range (4–9) for organic pollutants degradation (Cai et al., 2016). Thus,  $\text{SO}_4^{\cdot-}$ -based AOPs were more attractable.  $\text{SO}_4^{\cdot-}$  can be produced from persulfate (PS,  $\text{S}_2\text{O}_8^{2-}$ ) and peroxymonosulfate (PMS,  $\text{HSO}_5^-$ ) with the activation effect of heat, ultraviolet (UV) light radiation, ultrasound and pH conditions of aqueous solution (Devi et al., 2016). Generally, PS is applied more widely since it is cheaper than PMS. However,  $\text{SO}_4^{\cdot-}$ -based AOPs are limited in practical due to the high energy input and costs for PS/PMS activation (Tan et al., 2012; Mahdi-Ahmed and Chiron, 2014). So more economical and efficient activation method should be explored.

Recently, transition metal-mediated PS activation has received great attention. Transition metal ion such as  $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Cu}^{2+}$  were found to be effective to activate PS and produce  $\text{SO}_4^{\cdot-}$  for the contaminant degradation (Anipsitakis and Dionysiou, 2004). In addition, it is reported that the oxidation efficiency of  $\text{Fe}^{2+}$ /PS process could be enhanced due to the promoted conversion of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  induced by UV irradiation (Khan et al., 2013). Unfortunately, the homogenous activation of PS has many drawbacks, for instance, difficult recovery of catalyst, accurate stoichiometric amounts for catalyst and potential biological toxicity of transition metal ion catalysts. In order to overcome these disadvantages, solid transition metal oxides have been as the substitute. Iron oxides (Yan et al., 2011), copper oxides (Du et al., 2017) and manganese oxides (Wang et al., 2015) all are proven to activate PS, further achieving the effective degradation of organic pollutants. Heterogeneous catalyst instead of homogeneous catalyst not only decrease the operation costs by the recycle of catalyst, but also avoid the second pollution induced by the higher metal ions leaching in the homogenous reaction (Liang et al., 2017; Li et al., 2016). As a low-cost heterogeneous catalyst, layered double hydroxides (LDHs) have been widely investigated due to the inherent merits of large specific surface area, special structure and relatively simple synthesis process (Yue et al., 2017). Yan et al. (2017) fabricated CuMgFe-LDH through the co-precipitation method and the composite was an efficient PS activator, resulting in 93.7% ethylbenzene degradation efficiency and 65.2% TOC removal efficiency in 24 h. The visible light has been proposed as promising cost-effective alternative to replace UV light, which only covers about 5% of the whole sunlight (Kulkarni et al., 2015). Our previous research showed that ZnFe-LDH had excellent photocatalytic capacity for methylene blue and tetracycline degradation under visible light (Yang et al., 2017). Therefore, it can be expected that the combination of LDH-based catalyst with PS could enhance the photo-degradation of bio-recalcitrant organic contaminants under visible-light irradiation. However, to the best of our knowledge, the relevant reports are scarcely.

In this study, we used a common solid catalyst CuFe-LDH to heterogeneously activate PS under visible-light irradiation. Transition metals copper (II) and iron (III) complexes in CuFe-LDH maybe play important role in the enhancement of photocatalytic ability. Firstly both  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and  $\text{Cu}^{2+}/\text{Cu}^{3+}$  pairs effectively activate PS to produce  $\text{SO}_4^{\cdot-}$ . Additionally, the enhanced redox cycle of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and  $\text{Cu}^{2+}/\text{Cu}^{3+}$  with the assistance of visible-light irradiation also accelerates the reaction rate. The photogeneration sulfate radical potential of CuFe-LDH was evaluated through the decoloration of cationic dye methyl violet (MV) under visible-light irradiation. In addition, kinetic studies were conducted for a better understanding of the influence of catalyst dosage, PS concentration, initial pH, and coexisting ions on the MV degradation. Finally, underlying mechanism for the enhanced generation of free radicals and MV degradation in CuFe-LDH/PS/Vis system was preliminarily elucidated as well.

## 2. Materials and methods

### 2.1. Chemicals

Potassium peroxydisulfate ( $\text{K}_2\text{S}_2\text{O}_8$ , 99.5%), methyl violet dye ( $\text{C}_{25}\text{H}_{31}\text{N}_3$ ), copper (II) nitrate trihydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , 98.5%), iron (III) nitrate nonahydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , 98.5%), sodium hydroxide (NaOH, 99.0%), sodium carbonate anhydrous ( $\text{Na}_2\text{CO}_3$ , 99.0%), methanol ( $\text{CH}_3\text{OH}$ , 99.5%), ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ , 99.7%), tert-butyl alcohol ( $\text{C}(\text{CH}_3)_3\text{OH}$ , 99.0%), sodium chloride (NaCl, 99.5%), sodium sulfate anhydrous ( $\text{Na}_2\text{SO}_4$ , 99.0%) were all analytical grade and purchased from Ainopharm Chemical Reagent Co., Ltd. 0.1M  $\text{HNO}_3$  and 0.1M NaOH were used to adjust the solution pH. Methanol was used as the quenching reagent to avoid further reaction before chemical analysis.

### 2.2. Catalyst preparation

The catalyst CuFe-LDH was prepared by the modified co-precipitation method (Zubair et al., 2017). Specifically,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (7.5 mmol) and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (2.5 mmol) were completely dissolved in 60 mL de-ionized (DI) water with vigorous stirring, which defined as solution A. Meanwhile, solution B was also prepared through dissolving NaOH (20 mmol) and  $\text{Na}_2\text{CO}_3$  (5 mmol) in the 60 mL DI water. Solution A and B were simultaneously added dropwise in a 250 mL three mouth flask at  $\text{pH } 4.4 \pm 0.2$  with magnetic stirring. After titrations finished, the mixture was stirred for 0.5 h and then heated in a stainless steel reactor at  $110^\circ\text{C}$  for 5 h. At last, the precipitates were filtered and washed with DI water until the supernatant liquid was neutral. The collected solids were dried at  $65^\circ\text{C}$  for 24 h and denoted as CuFe-LDH ( $\text{Cu}^{2+}/\text{Fe}^{3+}$  molar ratio 3:1).

### 2.3. Catalyst characterization

The crystallographic properties of the fabricated samples were determined by X-ray diffractometer (XRD) on a Rigaku D/max 2500v/pc ( $\text{Cu}$ ,  $\text{K}\alpha$ ,  $\lambda = 0.154\text{ nm}$ , 40 kV, 40 mA) at a scan rate of  $0.1^\circ 2\theta\text{s}^{-1}$ . Fourier transform infrared spectroscopy (FTIR) was measured on an IR Prestige-21 spectrometer by the standard KBr disk method. The particle morphological analysis was performed using field emission scanning electron microscopy (FESEM, Hitachi S-4800) with 5.0 kV scanning voltages. The UV–vis diffuse reflectance spectrum was obtained by a UV–vis spectrometer (UV-4100, Shimadzu) with  $\text{BaSO}_4$  as the reference. Electron spin resonance (ESR) spectra were examined on a Bruker ER200-SRC spectrometer with 5,5-Dimethyl-1-pyrrolidine-N-oxide (DMPO) as the spin-trapping agent.

### 2.4. Catalytic degradation experiment

The photogeneration sulfate radical potential of CuFe-LDH (3:1) was evaluated through cationic dye methyl violet (MV) decomposition under a Xe lamp (300W) with a 420 nm cut filter (light intensity:  $100\text{ mW cm}^{-2}$ ). In a typical run, 20 mg catalysts were dispersed in 100 mL MV solution with initial concentration of 20 mg/L. To establish the adsorption-desorption equilibrium between the catalyst and dyes, the solution firstly kept in the dark conditions for 30 min with constant magnetic stirring (around 500 rpm) before the photocatalytic process was initiated. After the addition of 20 mg PS, the resultant mixture was immediately exposed to visible light. At appropriate time intervals (3 min), 1.5 mL liquid samples were collected and quickly mixed with 2.5 mL methanol to quench the reaction. Subsequently, the samples were centrifuged at 10,000 rpm for 10 min. The residual MV concentration was determined using a Shimadzu UV–vis spectrophotometer at the wavelength of 590 nm. All the experiments were conducted in an air-conditioned room ( $25 \pm 2^\circ\text{C}$ ) in duplicates and mean values were reported.

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