



Degradation of Crystal Violet by catalytic ozonation using Fe/activated carbon catalyst



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ABSTRACT

An Fe/activated carbon catalyst was prepared and used in catalytic ozonation of Crystal Violet. The catalyst was characterized by SEM and XRD, and the results showed that the iron loaded on activated carbon existed in α -FeOOH phase. An improved effect was achieved in the decolorization of Crystal Violet via catalytic ozonation in the presence of Fe/activated carbon compared with ozonation alone. Almost complete decolorization (>96%) of 400 mg/L Crystal Violet was achieved after 30 min reaction under the conditions of 4.44 mg/min ozone dosage, 300 mL/min gas flow rate, 2.5 g/L catalyst dosage and pH 7, while 57% COD removal efficiency was obtained when the reaction time was prolonged to 90 min. The acute toxicity to *Daphnia magna* decreased during 90 min of catalytic ozonation. The main intermediates were separated and identified by gas chromatography–mass spectrometry (GC–MS) technique and an initial degradation pathway of Crystal Violet was proposed.

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1. Introduction

The dye wastewater has long been a major environmental problem all over the world. The main sources of dye wastewater are from textile, dyeing, printing and other related industries [1,2]. Among various dyes, Crystal Violet, also known as C.I. Basic Violet 3, is a kind of cationic triphenylmethane dye. It is widely used for textile dyeing, paper printing, biological staining, dermatological agent, veterinary medicine, intestinal parasites and fungus, etc. [3,4]. Crystal Violet is a mutagen and mitotic poison, and its presence in water will cause a serious risk to aquatic life and constitute a potential human health hazard.

As one of the most effective methods, advanced oxidation processes (AOPs) have been used for the decolorization of Crystal Violet, including photo-catalysis [3–5], UV/H₂O₂ oxidation [6], Fenton and Fenton-like systems [6,7], electro-Fenton method [8,9] and electrochemical oxidation [10,11]. Compared with these AOPs, ozonation has proven to meet the strict color discharge limits of many industrialized countries [12–15]. It is well known that ozone is a strong oxidant, the oxidation potential of which is 1.52 times higher than that of chlorine [16]. Through a direct reaction of molecular ozone or a radical reaction involving the hydroxyl radical generated by the ozone decomposition, chromophoric dye

molecules can be broken into smaller non-chromophoric ones [17,18]. However, there are a few drawbacks which limit industrial applications of ozonation. First of all, the installation of ozone generation unit and the cost of electricity give rise to the high production cost of ozone [19]. Secondly, the poor mass transfer rate of ozone leads to the low ozone utilization. Furthermore, the limit oxidizing power of ozone ($E_0 = 2.07$ V) results in the low mineralization efficiency [20,21]. Fortunately, catalytic ozonation can improve the ozone utilization and mineralization degree through the transformation of ozone into more reactive species [16,22,23]. Activated carbon not only has excellent adsorption capacity, but also exhibits high catalytic activity due to its high surface area and surface chemical properties [17,24–26]. Metal oxides are also used for the catalytic ozonation [16], and iron type catalysts are normally employed due to their relatively low price and high catalytic activity [27–29]. Moreover, iron oxide loaded on the activated carbon could further improve the catalytic activity [30–32]. To the best of our knowledge, there is no report on the degradation of Crystal Violet by heterogeneous catalytic ozonation with Fe/activated carbon catalyst. Therefore, in this study, Fe/activated carbon was prepared and used for the catalytic ozonation of Crystal Violet. The effect of operation condition such as catalyst dosage, initial dye concentration, pH, temperature, gas flow rate and ozone dosage on the decolorization of Crystal Violet was investigated. The degradation of Crystal Violet in terms of COD removal and the variation of acute toxicity to *Daphnia magna* (*D. magna*)

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during the heterogeneous catalytic ozonation process were also investigated.

2. Materials and methods

2.1. Materials

The reagents used in this study were analytical grade. Crystal Violet ($C_{25}H_{31}N_3$) was obtained from Shenyang No. 3 Chemicals Reagent Factory (China) and used without further purification. Crystal Violet solution was prepared in a 0.05 mol/L phosphate buffer solution.

2.2. Catalyst preparation and characterization

The catalyst used in this study was iron oxide supported on activated carbon (AC), which was prepared by incipient wetness impregnation [33]. Activated carbon was subjected to pretreatment with HNO_3 and $NaOH$ to modify its porous structure and surface chemistry. Then one gram of dry based carbon was equilibrated with 30 mL 1.0 M N_2 -purged ferrous sulfate solution for 24 h to prevent the formation of iron hydroxide. After adsorption saturation, oxygen was bubbled through the slurry with magnetic stirring. The dispersion was then aged for 48 h, and the impregnated activated carbon samples were separated from the mixture, rinsed with de-ionized water for three times, and dried at 60 °C.

The morphology of samples was obtained using a scanning electron microscopy (Quanta 200, FEI, Netherlands). X-ray powder diffraction (XRD) analysis was investigated to identify the crystalline phases of Fe/activated carbon catalyst. Diffraction data were obtained by step-scans using $CuK\alpha$ radiation generated at 30 kV and 30 mA, scanning from 10° to 80° and a position-sensitive detector using a step size of 0.02°. The pH at the point of zero charge (pH_{pzc}) was measured with a mass titration method [32].

2.3. Methods

In each run, Fe/activated carbon was added into the reactor containing 100 mL solution. The mixture was then stirred at 500 r/min for 30 min to reach adsorption equilibrium [33]. Thereafter, ozone was continuously bubbled into the solution. Ozone was generated by using an ozone generator (XFZ-5BI, China). The gas flow rate Q was determined with a bubble flow meter. The gaseous ozone concentration $[O_3]_g$ was monitored by the iodometric method with potassium iodide solution [34]. At pre-selected time intervals, 1 mL sample was withdrawn from the reactor and then filtered through 0.45- μ m membrane filter before analysis.

The absorbance of the sample was measured at $\lambda_{max} = 584$ nm using a Shimadzu UV-1600 spectrophotometer (Shimadzu, Japan). Decolorization efficiency was calculated according to Eq. (1):

$$\text{Decolorization efficiency (\%)} = (A_0 - A_t)/A_0 \times 100\% \quad (1)$$

where A_0 and A_t are the absorbencies at time 0 and t , respectively.

Chemical oxygen demand (COD) was determined using closed reflux spectrophotometric method based on the Standard of the People's Republic of China for Environmental Protection [35].

The intermediate products during the reaction were detected by gas chromatography–mass spectrometry (GC–MS) (Shimadzu GCMS-QP2010 Plus). Samples for GC–MS analysis were prepared as follows [7,11]: 100 mL dye solution was extracted with dichloromethane (total volume 100 mL) ten times, and the extracts were then concentrated by rotary evaporator at 40 °C to about 1 mL before being analyzed by GC–MS. A HP-5 MS capillary column

(30 m length \times 0.25 mm ID \times 0.25 μ m film thickness) was employed for GC separation. The GC equipment was operated in a temperature programmed mode with an initial temperature of 40 °C held for 4 min, then ramped first to 80 °C with a 4 °C min^{-1} rate and held for 2 min; then ramped to 280 °C at 8 °C min^{-1} and held at that temperature for 9 min. Helium was used as a carrier gas at a flow rate of 5.79 mL min^{-1} . Electron impact (EI) mass spectra were scanned from 10 to 300 m/z. The injector, ion source and interface temperatures were set at 280, 220 and 280 °C, respectively.

The active toxicity was determined with *D. magna* immobilization test [36]. *D. magna* was cultured in laboratory for more than three generations. The acute toxicity experiments were repeated four times using 24-h-old *D. magna* in 100-mL-capacity test beakers. They were set in the incubator along with testing samples. The incubator was kept at 20 °C in a 16 h light-8 h dark cycle. No food was given during the acute toxic test. Surviving and mobile *D. magna* was counted after 24 h.

3. Results and discussion

3.1. Characterization of the catalysts

A small amount of iron oxide (56 mg g^{-1} Fe content) was immobilized on the activated carbon, and the catalysts with diameters of 250–300 μ m were used in the catalytic ozonation processes. The results of textural properties for Fe/activated carbon catalyst were given in Table 1, and the SEM images of the fresh catalyst sample were shown in Fig. 1. It can be seen that the catalyst had an irregular surface (Fig. 1a), and some large druses (small spherical particles, the average particle size was about 10 μ m) were dispersed in the uneven surface (Fig. 1b). Fig. 2 displayed X-ray powder diffraction patterns of Fe/activated carbon catalyst. The main diffraction peaks located at 21.30°, 34.72°, 41.16°, 58.94° and 61.44° of 2θ corresponded to α -FeOOH [37], supposing a high catalytic activity for Fe/activated carbon catalyst in the ozonation process [38–44].

3.2. The effect of catalyst dosage

In order to determine the effect of the catalyst dosage on the decolorization of Crystal Violet by heterogeneous ozonation process, experiments were performed at various catalyst dosages. As can be seen in Fig. 3, catalytic ozonation could achieve higher decolorization rate than ozonation alone. The α -FeOOH has three different types of surface functional groups ($\equiv Fe-OH_2^+$, $\equiv Fe-OH$, and $\equiv Fe-O^-$) depending on the solution pH, which could enhance ozone decomposition to generate hydroxyl radicals via the following reactions [38,44,45],

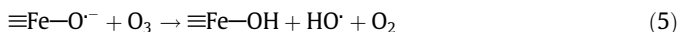
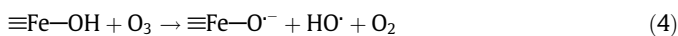
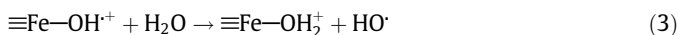
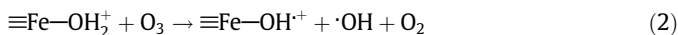


Table 1

The textural properties of the Fe/activated carbon catalysts.

Catalysts	Particle size (μ m)	Textural properties		
		BET area (m^2/g)	Pore volume (cm^3/g)	Average pore size (nm)
Fe/AC	250–300	195.0	0.1645	3.374

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