ELSEVIER

Journal of Hazardous Materials B125 (2005) 96–101

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

Decolorization and mineralization of a phthalocyanine dye C.I. Direct Blue 199 using UV/H_2O_2 process

Hung-Yee Shu*, Ming-Chin Chang

Department of Environmental Engineering, Hungkuang University, No. 34 Chung-Chie Road, Shalu, Taichung County, Taiwan 433, ROC

Received 28 February 2005; received in revised form 27 April 2005; accepted 2 May 2005
Available online 27 June 2005

Abstract

In this study, the successful decolorization and mineralization of phthalocyanine dye (C.I. Direct Blue 199, DB 199) by an advanced oxidation process (AOP), UV/H_2O_2, were observed while the experimental variables such as hydrogen peroxide dosage, UV dosage, initial dye concentration and pH were evaluated. The operating conditions for 90% decolorization of C.I. DB 199 and 74% removal of total organic carbon (TOC) were obtained for initial dye concentration of 20 mg l^{-1}, hydrogen peroxide dosage of 116.32 mM, UV dosage of 560 W and pH of 8.9 in 30 min. The pseudo-first order rate constant is a linear function of reverse of initial dye concentration. They linearly increased by incrementing UV dosage, yet were non-linear enhancement by increasing the hydrogen peroxide concentration. A higher pseudo-first order rate constant about 0.15 $\min^{-1}$ was observed while hydrogen peroxide concentration within 5.82–116.32 mM. Moreover, the decolorization of C.I. DB 199 was observed to be more difficult than that of an azo dye, C.I. Acid Black 1, under the same operating conditions.

Keywords: Ultraviolet; Advanced oxidation processes (AOPs); UV/H_2O_2; Phthalocyanine dye; Decolorization; Mineralization

1. Introduction

The major concern of wastewater treatment of textile dyeing and finishing industry is the residue dye contents from dyeing process, which results into high levels of environmental contamination such as color intensity and chemical oxygen demand (COD) of effluents. Most of the dyestuffs with complicated aromatic structures are designed to be highly resistant to microorganism so that biological wastewater treatment processes are very inefficient in treating of these dyes. Some studies [1–3] proved that the dyes were readily non-biodegraded under aerobic conditions. Otherwise, most of the textile industries using the traditional chemical coagulation and activated sludge process for wastewater treatment cannot pass the more restricted color criteria, unfortunately [4]. That implies textile dyeing industries should pursue more efficient technique to be the pre-treatment or polishing processes to decolorize the highly colored wastewater.

There are various types of synthetic dyes used in textile industries such as azo, anthraquinone, triarylmethane and the phthalocyanine (PC) groups while azo dyes are in the largest class of dyes used commercially and PC groups are employed mainly for blue and green dyes. In this work, the target compound C.I. Direct Blue (DB) 199 is one of the copper phthalocyanine (CPC) dyes, which are usually produced by connecting the solubilizing functional groups to PC structure. CPC dyes are utilized extensively in versatile textile dyeing and paper industry such that C.I. DB 199 is widely used in cotton dyeing, also paints and varnishes industry, as well as inkjet printer cartridge. The UV/H_2O_2 process was frequently applied to degrade refractory organics in aqueous phase [5–16] concomitant with small reactor volume requirement, powerful oxidation ability, high decomposition efficiency, low toxic intermediates and no sludge production, etc. Recently, many investigators reported the successful applications of the UV/H_2O_2 process for dye wastewater treatment. Shu et al. [6] demonstrated that it effi-

---

* Corresponding author. Tel.: +886 4 26318652x4111; fax: +886 4 26525245.
E-mail address: hyshu@sunrise.hk.edu.tw (H.-Y. Shu).

0304-3894/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2005.05.016

ciently decolorized Acid Red 1 and Acid Yellow 23. Galindo and Kalt [7] showed effectively color removal of Acid Orange 7 by UV/H_2O_2 process. Similar results obtained by Neamtu et al. [8] presented successfully decolorizing three reactive azo dyes, C.I. Reactive Yellow 84, C.I. Reactive Black 5 and C.I. Reactive Red 120. On the other hand, the effect of hydrogen peroxide dosage on decolorization for dyes by UV/H_2O_2 process was discussed by Ince [9] and Aleboyeh et al. [10]. Both of the investigations observed an optimal hydrogen peroxide concentration existed for decolorization of azo dye. While overdosing hydrogen peroxide, the decolorization rate decreased substantially. Besides, Mohey El-Dein et al. [11] developed a kinetic model to describe the decolorization behavior of Reactive Black 5 by the UV/H_2O_2 process. They investigated that the effects of H_2O_2 concentration and UV intensity affected the observed kinetic rate coefficients. Similarly, many other researchers took advantage of this process on the azo dye removal in the laboratory batch reactors [12–16]. In addition to the azo dyes, few researches involve the decolorization of other dyes by UV/H_2O_2 process. However, Heinfling et al. [17] reported that a phthalocyanine dye, Reactive Blue 38, was decolorized by the ligninolytic peroxidases of various fungal species with hydrogen peroxide. Hunag et al. [18] showed preliminary effective results of decolorizing phthalocyanine dye in dyeing effluent by both ozonation and UV/H_2O_2 processes. Little attention has been given to the decolorization of PC dyes by advanced oxidation processes (AOPs).

The aim of this study was to evaluate the feasibility of decolorizing and mineralizing phthalocyanine dye wastewater containing C.I. DB 199 by UV/H_2O_2 process. The operating parameters such as hydrogen peroxide dosage, UV dosage, initial dye concentration and pH were determined to find the suitable operating conditions for the best efficiencies of the color removal and TOC mineralization. Besides, the kinetic rate constants of C.I. DB 199 by UV/H_2O_2 process were calculated, which were also compared to those of azo dyes.

2. Experimental

The dye, C.I. Direct Blue 199 ($C_{32}H_{14}CuN_8O_6S_2\cdot Na\cdot NH_4$, molecular weight 775.17, characteristic wavelength 594 nm, DB 199), chemical structure shown in Fig. 1, was obtained from Lyntech Industries Inc., Lyndhurst, NJ, USA and used without further purification. Hydrogen peroxide was obtained from Fluka Chemical with 35% (w/w) concentration.

A New England Photochemical Co. Model RPR-100 photochemical reactor was employed for the decolorization and mineralization study of C.I. DB 199. There were 16 RPR-1849/2537 Å low pressure mercury arc UV lamps (wavelength 253.7 nm, 35 W/lamp) fixed along the inner wall of reactor that makes the maximum UV power of 560 W in a 500 ml quartz stirred vessel. The detail description of reactor configuration and operation were published in our previous paper [15]. Samples were withdrawn at time intervals and analyzed by the spectrophotometer of Varian DMS 200 UV–visible with the single wavelength absorbance at 594 nm, as well as TOC analyzed with IO Analytical 700 TOC analyzer.

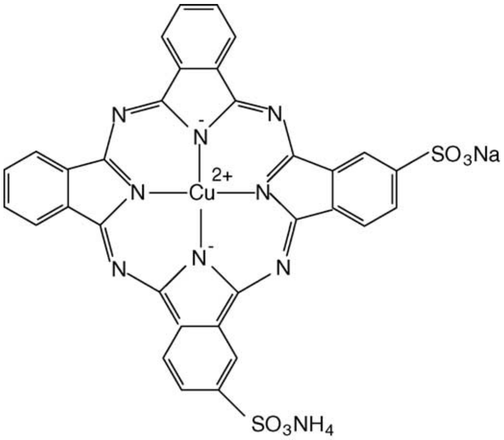

Fig. 1. Structure of C.I. Direct Blue 199 (C.I. 74180).

3. Results and discussion

In the photochemical reactor, the decolorization and mineralization of C.I. DB 199 were conducted using the UV/H_2O_2 process under various operating conditions such as initial hydrogen peroxide concentration, UV light power and initial dye concentration. In this process, UV irradiates the hydrogen peroxide to produce the strongest oxidizing free radicals such as hydroxyl and peroxyl radicals, which attack the organics instantaneously as soon as the reaction starts, to degrade the target compound. Besides, the decolorization rate expression of C.I. DB 199 can be simplified as a pseudo-first order kinetic model as follows [15],

$$-\frac{dC_A}{dt} = k_{obs}C_A \quad (1)$$

where k_{obs} denotes a pseudo-first order kinetic constant, C_A the concentration of C.I. DB 199 and t represents time.

3.1. Effect of initial hydrogen peroxide concentration

Many researches have evaluated the decolorization of various dyestuffs in aqueous solutions by UV/H_2O_2 process [6–9] that the initial H_2O_2 concentration played a very important role for the generation of hydroxyl radicals to decolorize dyes. In the experiment, the time courses of C.I. DB 199 decolorization by UV/H_2O_2 process under various H_2O_2 concentrations are shown in Fig. 2. The observed pseudo-first order rate constants of reactions were calculated by linear regression of the rate expression Eq. (1), that were plotted versus concentrations of H_2O_2 shown in Fig. 3. The effect