Decolorization and mineralization of a phthalocyanine dye C.I. Direct Blue 199 using UV/H$_2$O$_2$ process

Hung-Yee Shu [*], Ming-Chin Chang

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

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$_2$O$_2$, 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.
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Keywords: Ultraviolet; Advanced oxidation processes (AOPs); UV/H$_2$O$_2$; 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$_2$O$_2$ 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$_2$O$_2$ 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).

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 ($C_{32}H_{14}CuN_8O_6S_2$·Na· 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
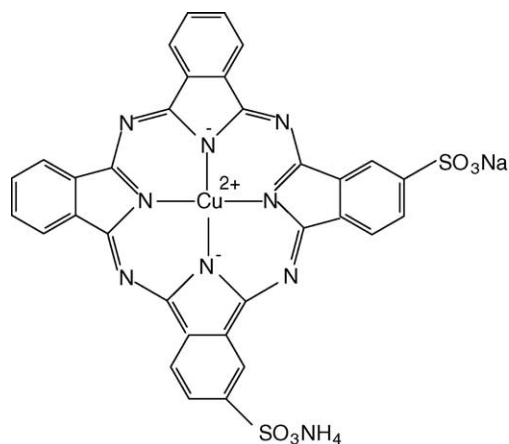

Fig. 1. Structure of C.I. Direct Blue 199 (C.I. 74180).

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.

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],

$$-\frac{dC_A}{dt} = k_{obs}C_A \tag{1}$$

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
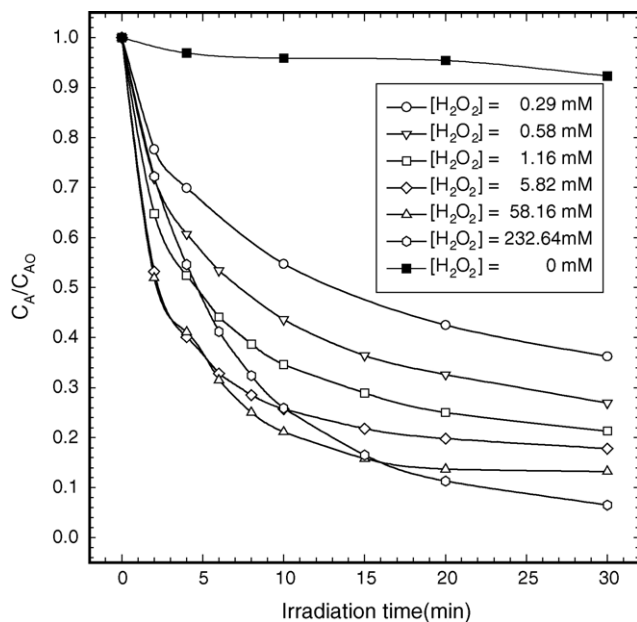
Fig. 2. The normalized concentration (C_A/C_{A0}) of C.I. Direct Blue 199 vs. irradiation time as a function of initial hydrogen peroxide concentration for 20.0 mg l^{-1} of initial dye concentration and 560 W of UV input power.

of direct UV irradiation was insignificant. The color removal efficiency at irradiation time of 30 min without hydrogen peroxide addition was only 7.7% and the observed first order rate constant was 0.0028 min^{-1}. For reaction combined UV irradiation and hydrogen peroxide addition, the decolorization was extremely powerful than that of direct photolysis. The decolorization rates increase linearly by incrementing the H$_2$O$_2$ concentrations from 0.29 to 5.82 mM. Once passing
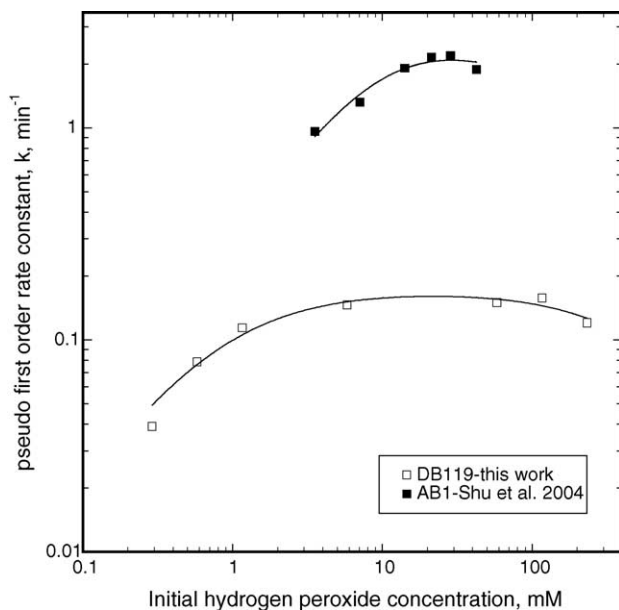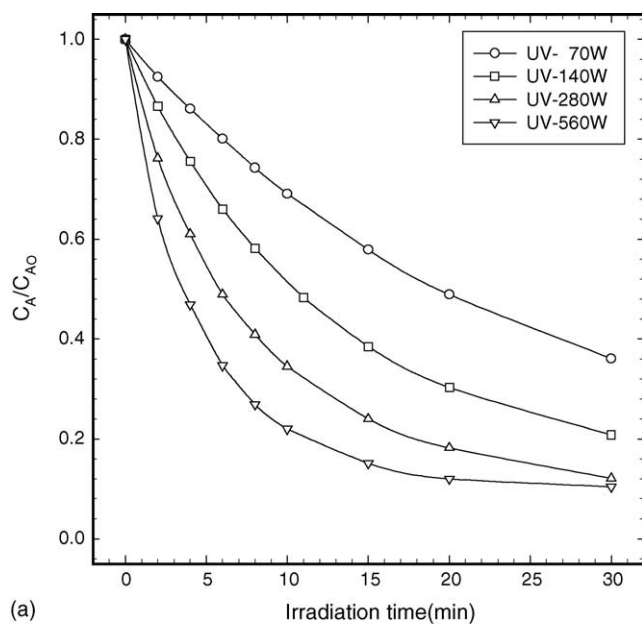

Fig. 3. Observed pseudo-first order rate constants vs. initial hydrogen peroxide concentration for two dyes. DB 119 denotes C.I. Direct Blue 119 and AB 1 denotes C.I. Acid Black 1 from our previous work [15].

5.82–116.32 mM, the rates attained to the maximum. However, the rate constant decreases from 0.1575 to 0.1204 min^{-1} significantly while concentration of H$_2$O$_2$ was greater than 116.32 mM. Explanation of this scenario was that increase of H$_2$O$_2$ concentration may be counterbalanced because that the hydroxyl radicals are scavenged by H$_2$O$_2$. It means the excess dosage of H$_2$O$_2$ reacts with hydroxyl radicals so that it competes with dye for the radicals in the photolysis at the same time. Therefore, the H$_2$O$_2$ concentration observed for the maximum C.I. DB 199 decolorization was 116.32 mM. In comparison with our previous work [15], the pseudo-first order decolorization rate constants of C.I. DB 199 are about 10 times less than that of the azo dye C.I. Acid Black 1 (AB 1) in the same UV/H$_2$O$_2$ process which employed 560 W of UV intensity and initial dye concentration of 20 mg l^{-1}. The largest rate constants obtained by the best conditions of initial concentrations of H$_2$O$_2$ were 5.82–116.32 mM for C.I. DB 199, narrower operating window of 14.06–28.56 mM for C.I. AB 1, respectively.
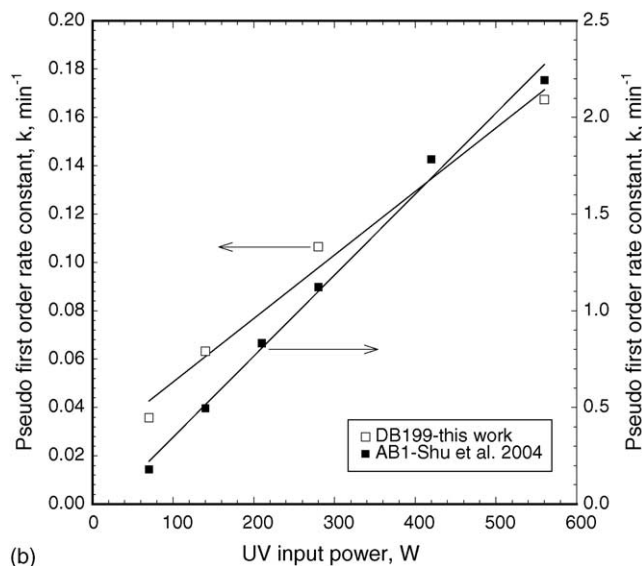
3.2. Effect of UV light power

In addition to the concentration of H$_2$O$_2$, the UV light intensity affects the UV/H$_2$O$_2$ reaction for decolorization of C.I. DB 199 as well. Decolorization efficiency was nearly negligible while in the presence of H$_2$O$_2$ without UV radiation. The time courses of C.I. DB 199 decolorization by UV/H$_2$O$_2$ process under various UV input powers for the initial H$_2$O$_2$ concentration of 116.32 mM are shown in Fig. 4(a). The decolorization ratios increased by raising the UV input power. The observed pseudo-first order rate constant of reaction versus UV power is shown in Fig. 4(b), which was a nearly linear relationship between k_{obs} and UV dosage. Theoretically, the higher decolorization rates form by the higher UV powers owing to the faster formation of free radical so that the k_{obs} increases in the same initial H$_2$O$_2$ concentration. However, the disadvantage of UV/H$_2$O$_2$ process is the poor absorption of H$_2$O$_2$ in UV region so that the amount of UV radiation absorbed by H$_2$O$_2$ plays an important role in the formation of plentiful radicals to enhance the dye decolorization. Although C.I. AB 1 [15] was easier to be decolorized than C.I. DB 199, both the decolorization rate constants were linear increased with respect to UV intensity.

In addition to the color, TOC is also one of the major pollution indicators for dye wastewater. From above results, the decolorization of C.I. DB 199 was shown effectively by UV/H$_2$O$_2$ process. Meanwhile, the effectiveness of mineralization was evaluated by this process as well, that total organic carbon (TOC) of dye wastewater was reduced during the reaction shown in Fig. 5. However, the mineralization efficiency increased while increasing UV power though, the mineralization was not as effective as decolorization. As shown in Figs. 4(a) and 5, in comparison with decolorization efficiency were 89.6 and 87.9% while TOC removal efficiency were 73.8 and 51.9% at 30 min of reaction time for UV power at 560 and 280 W, respectively. The variable profile in the begin-

(a)

Fig. 5. The normalized TOC (TOC/TOC_0) of C.I. Direct Blue 199 vs. irradiation time as a function of various UV input power for 20.0 mg l^{-1} of initial dye concentration. The initial TOC of this synthesized dye wastewater was 6.06 mg l^{-1}.

3.3. Effect of initial dye concentration

The time courses of C.I. DB 199 decolorization by UV/H_2O_2 process are shown in Fig. 6(a) for different initial dye concentration within 20.0–80.0 mg l^{-1}. Additionally, the effect of initial dye concentration on the decolorization rate (k_{obs}), which declines significantly by raising initial dye concentration, is shown in Fig. 6(b). Besides, the TOC reduction by time course of C.I. DB 199 using UV/H_2O_2 process is shown in Fig. 7, which expresses the decreasing efficiency of mineralization by increasing initial dye concentration. Thus, TOC removal efficiencies for initial dye concentration of 20 and 80 mg l^{-1} in 40 min were 77.1 and 60.8%, respectively.

3.4. Effect of pH

In general, raising pH results into reducing dye decolorization rates by UV/H_2O_2 process because that H_2O_2 generally dissociates into water and oxygen rather than hydroxyl radicals in alkaline condition [19]. The effect of pH on the pseudo-first order decolorization rate constant is plotted in Fig. 8. In the experiment, pH adjustment was conducted for comparison with the decolorization effect, that it raised to 7.2, 8.9 and 10.6 by adding 1.0N sodium hydroxide (NaOH) solution. Results show the observed decolorization rate (k_{obs}) of dye enhances by incrementing pH to 7.2 and 8.9, yet that it declined obviously once raising continuously pH to 10.6. Besides, one lower pH of 3.3 was employed by adding hydrochloric acid (HCl) to result into the rate significantly decreased than that of pH 4.9. This implies that a very narrow operation range for pH of 7.2–8.9 for high k_{obs} can be

(b)

Fig. 4. (a) The normalized concentration (C_A/C_{A0}) of C.I. Direct Blue 199 vs. irradiation time as a function of various UV input power. (b) Observed pseudo-first order rate constants vs. UV input power. The operating conditions were 20.0 mg l^{-1} of initial dye concentration and 116.32 mM of initial hydrogen peroxide concentration. DB 119 denotes C.I. Direct Blue 119 and AB 1 denotes C.I. Acid Black 1 from our previous work [15].

ning of reaction time in Fig. 5 to make TOC/TOC_0 residual larger than 1.0 may result from the decomposition of refractory organic compounds into small organic compounds that TOC analyzer detects more carbon signals from the refractory compounds before the total detection of oxidization by UV/H_2O_2 process. It took 30 min to reduce 73.8% of TOC for C.I. DB 199 for the initial TOC concentration of 6.06 mg l^{-1}. This implies the molecule of C.I. DB 199 is very complex and difficult to be oxidized into carbon dioxide.
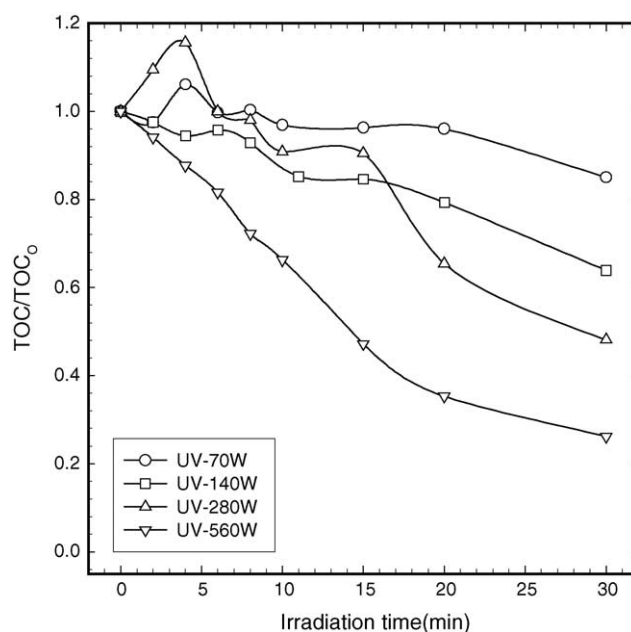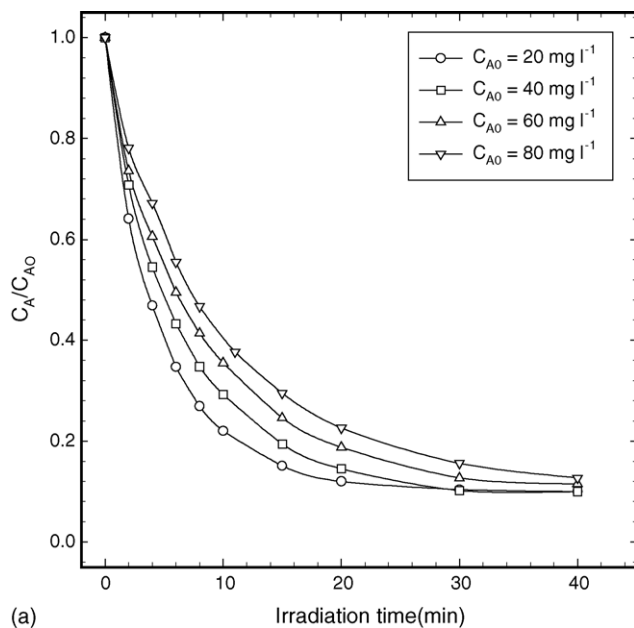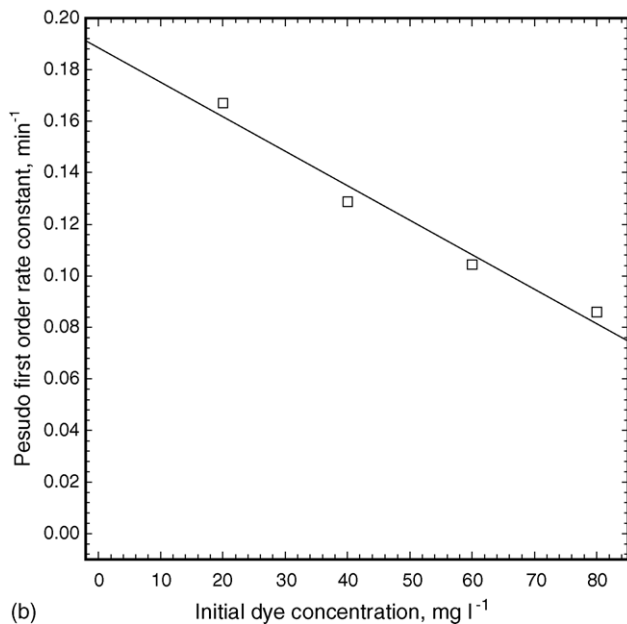
(a)

(b)

Fig. 6. (a) The normalized concentration (C_A/C_{A0}) of C.I. Direct Blue 199 vs. irradiation time as a function of initial dye concentration. (b) The observed first order rate constant as function of initial dye concentration. The operating conditions were 560 W of UV input power and 116.32 mM of initial hydrogen peroxide concentration.

obtained. Once the pH was greater than 8.9 or less than 4.9, the unsuccessful treatment of dye wastewater performed. Meanwhile, this experimental result of the highest k_{obs} for decolorizing C.I. DB 199 in the UV/H$_2$O$_2$ process was observed at pH 8.9. It is different from that of C.I. Acid Orange 52 and C.I. Acid Orange 7 at pH 2.8 and 3.8, respectively, by Galindo and Kalt [7]. Similarly, for the TOC reduction the highest efficiency of 83.5% was obtained at pH 8.9 among five pH conditions for 30.0 min of reaction time. However, pH of 3.3 and 10.6 performed the worst TOC reduction.
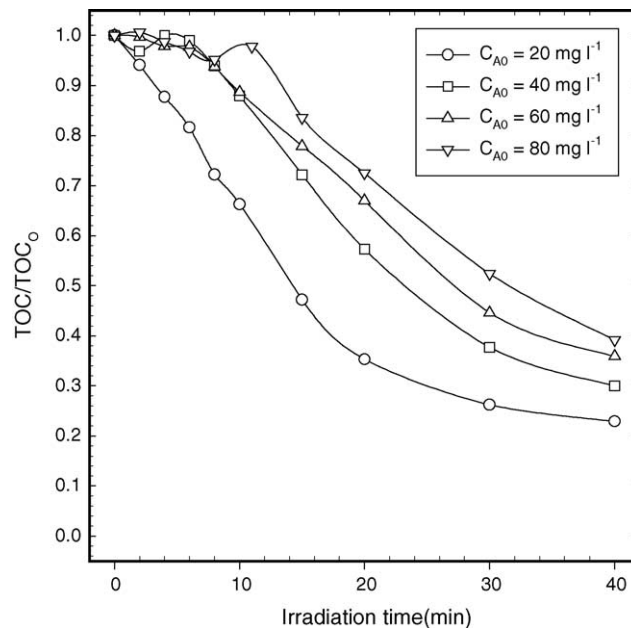

Fig. 7. The normalized TOC (TOC/TOC$_0$) of C.I. Direct Blue 199 vs. irradiation time as a function of initial dye concentration. The operating conditions were same as Fig. 6.
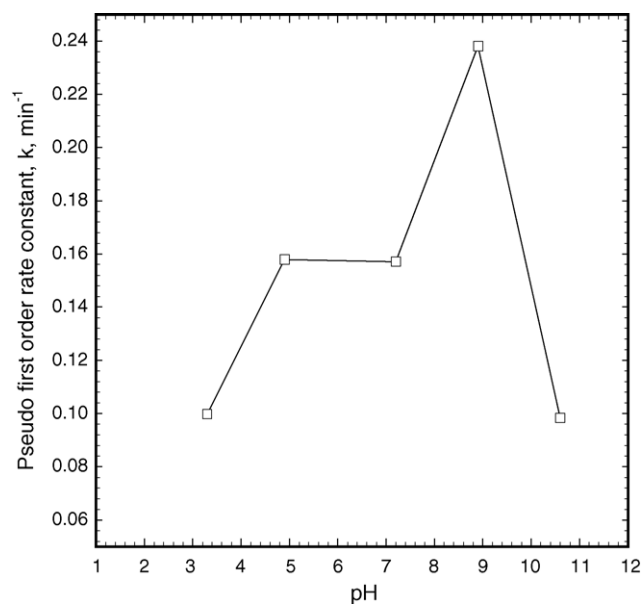

Fig. 8. The pseudo-first order rate constant vs. pH for initial dye concentration of 20.0 mg l^{-1} and initial hydrogen peroxide concentration of 116.32 mM. The UV input power was 560 W.

4. Conclusion

The experimental results showed that the UV/H$_2$O$_2$ process was a feasible pre-treatment method for decolorization as well as mineralization of phthalocyanine dye wastewater from textile industries under the suitable operating conditions. The decolorization rates of C.I. DB 199 were determined at different operational conditions such as UV dosage, hydrogen peroxide dosage, initial dye

concentration and pH. The 90% of dye decolorization can be reached within 30 min, while UV power of 560 W, H_2O_2 concentration of 116.32 mM and pH of 8.9. Therefore, both the greatest efficiency for color removal and mineralization were observed at above operational conditions. Besides, the pseudo-first order rate constant of decolorization of phthalocyanine dye C.I. DB 199 is about 10 times less than the azo dye C.I. AB 1 in the same reactor design and operating conditions. That implies that C.I. DB 199 is more difficult to be decolorized than C.I. AB 1.

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