Degradation of dyehouse effluent containing C.I. Direct Blue 199 by processes of ozonation, UV/H$_2$O$_2$ and in sequence of ozonation with UV/H$_2$O$_2$

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Abstract

The decolorization and mineralization of cotton dyeing effluent containing C.I. Direct Blue 199 (DB 199) by advanced oxidation processes (AOPs) such as ozonation, UV/H$_2$O$_2$, and in sequence of ozonation with UV/H$_2$O$_2$ processes were evaluated in this study. By ozonation alone, the color removal was almost 100% for DB 199 and greater than 80% for dye bath effluent rapidly within 5 and 15 min, respectively. Meanwhile, the reduction of total organic carbon (TOC) was about 60% for DB 199 and almost no change for dye bath effluent, respectively due to incomplete mineralization. On the other hand, by UV/H$_2$O$_2$ alone, the color removing not only took longer time but obtained lower removal efficiencies for DB 199 and dye bath effluent about 80% and 95% in 30 and 120 min, respectively. Nevertheless, it was more effective than ozonation for TOC removal while about 75% and 80% in 30 and 120 min, respectively. As a result, this study conducted the combination with the above two processes in order to shorten time demand as well as the higher removal efficiencies of both color and TOC simultaneously. Thus, the sequence process was designed to begin with ozonation to rapidly remove color proficiently, following by UV/H$_2$O$_2$ in order to promptly remove remaining TOC efficiently. The successful process design by sequence of ozonation with UV/H$_2$O$_2$ has proved the significant improvement for the removal of both color and TOC in dye bath effluent shortly. Besides, the lab prepared dye solution was substantially much easier to be decolorized than field dye bath effluent so that the lab results were utilized to design the further applications of pilot or full scale.
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Keywords: Advanced oxidation processes (AOPs); Ozonation; Direct Blue 199; Dye bath; Decolorization; Mineralization; TOC

1. Introduction

Effluents discharged from textile dyeing and finishing industries are recalcitrant by biological, chemical or physical treatment because of high organic contents and strong color, as well as surfactants containing and some other additives [1,2]. They are incapable to meet the effluent standards by traditional activated sludge process so that cause serious environmental pollution.

Advanced oxidation processes (AOPs), such as ozonation, UV/H$_2$O$_2$, UV/O$_3$ and UV/O$_3$/H$_2$O$_2$ have been proved to be powerful and widely used to treat the organic pollutants of industrial wastewater owing to be able to mineralize the organic contaminants into carbon dioxide and water [3]. Their decolorization ability for synthesized dye wastewater has been investigated to be successfully efficient by various researchers [4–11], who studied on the laboratory scale. For example, Shu and Huang [4] presented using ozonation and ultraviolet induced ozonation for the color removal of C.I. Acid Orange 10. Chen [5] showed that the decolorization of methyl orange was much more affected by both the concentrations of dye and ozone than other operation variables such as pH, temperature, agitation rate. Mohey El-Dein et al. [6] reported that C.I. Reactive Black 5 was decolorized by UV/H$_2$O$_2$ process while an optimum molar ratio of H$_2$O$_2$/dye. Many other literatures [7–11] investigated the decolorization of various dyes by UV/H$_2$O$_2$ process and they found it efficient for laboratory prepared pure dye solutions, while it was seldom reported for industrial textile effluents. Kunz et al. [12] proposed the application for industrial effluents by the sequential process of *Phanerochaete chrysosporium*–ozone that showed the good decolorization and phenol removal, yet insignificant total organic carbon

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reduction. Besides, the ozonation showed more powerful for decolorization of textile effluents than that of UV/H$_2$O$_2$ process [13]. Though the TOC destruction by ozonation was reported to be ineffective [14], that only 7% of TOC removal of a dye manufacturing wastewater was obtained by ozonation. Moreover, the unit or combination of process, such as ozonation, UV/H$_2$O$_2$, UV/O$_3$, Fe^{2+}/H$_2$O$_2$ and UV/O$_3$/H$_2$O$_2$, was studied by Azbar et al. [15] for COD and color removal of fiber dyeing effluent. The combination of UV/O$_3$/H$_2$O$_2$ was the most efficient process for both decolorization and mineralization of textile effluents. Thus, the above process was suggested to struggle against the removal problem of color and TOC at the same time in textile effluent.

The objective of this work was to study the feasibility of color and TOC removal by ozonation, UV/H$_2$O$_2$, and in sequence process of ozonation with UV/H$_2$O$_2$ for the dye bath effluent of textile industry. While the decolorization rate constants, which follow the pseudo-first-order reaction with respect to the dye concentration, were calculated for dye bath effluent and synthesized dye wastewater among the processes. The calculated constants were employed to evaluate the performance among the three processes.

2. Experimental

2.1. Material

Hydrogen peroxide was purchased from Fluka Chemical (30%, w/w). C.I. Direct Blue 199 (C$_{32}$H$_{14}$CuN$_8$O$_6$S$_2$·Na·NH$_4$, Characteristic wavelength 594 nm, Molecular weight 775.17, DB 199), chemical structure shown in Fig. 1, was obtained from Lyntech Industries Inc., Lyndhurst, NJ, USA, that used without further purification. Wastewater employed in this study was collected from dye bath effluent of a cotton fiber dyeing process with TOC of 131 mg l^{-1}, ADMI color of 780 units, adsorbance at 594 nm of 0.325 and pH of 6.8. Ozone was generated onsite from a Welback T-816 ozone generator in 5% concentration.
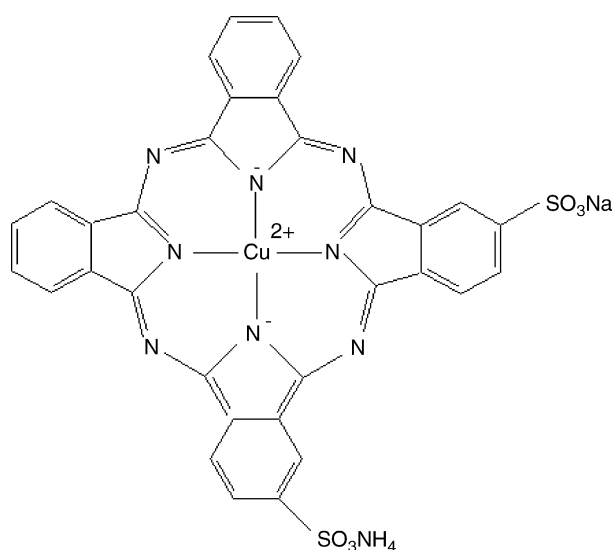

Fig. 1. Structure of C.I. Direct Blue 199.

2.2. Apparatus

In ozonation, an ozone contact reactor was designed for excellent mass transfer of ozone throughout wastewater that ozone gas was introduced into the bottom of reactor through a two-head sparger of medium porosity. The configuration of reactor was a cylindrical glass reactor by i.d. of 110 mm and height of 250 mm with 2.4 l holdup volume, yet at 2.0 l operated capacity. Ozone was generated from oxygen by Welsbach T-816 ozone generator, which produced fine ozone bubbles by flowing 6 l min^{-1} of 99.5% high purity oxygen or air into it while the maximum capacity of 110 W and 105 V.

A New England Photochemical Co., Model RPR-100 photochemical reactor was employed in this study to conduct the UV/H$_2$O$_2$ process. The reactor was fitted with 16 low pressure mercury arc UV lamps (wavelength 253.7 nm, 35 W/lamp) to irradiate total energy of 560 W on a 500 ml quartz stirred vessel. The more detail description of reactor configuration was omitted since it has been published in our previous paper [16]. Samples were withdrawn at time intervals and analyzed by the spectrophotometer and TOC analyzer.

2.3. Analyses

An IO Analytical 700 TOC analyzer was employed to detect the total organic carbon (TOC) of wastewater, which provided the estimation for the mineralization of dissolved organic compounds. The standard color detection procedure was developed by the American Dye Manufacturers Institute (ADMI). ADMI color index was employed to evaluate the color intensity of dye bath effluent. It was calculated by applying the Adams–Nickerson color difference formula, which substituted transmittance data obtained into 30 wavelengths, from 400 to 700 nm in every 10 nm interval. The above procedure followed the method 2120E of Standard Methods [17]. The optical absorption spectrum of synthesized C.I. DB 199 wastewater was determined by a Varian DMS 200 vis–UV spectrophotometer at its characteristic wavelength of 495 nm. Aqueous ozone concentration was measured by iodometric method proposed by Shechter [18]. Hydrogen peroxide concentration was determined by spectrophotometer method proposed by Masschelein et al. [19].

3. Results and discussion

From our preliminary studies [4,6], the kinetics of decolorizing dye wastewater by the processes of ozonation and UV/H$_2$O$_2$ were observed and simplified as a pseudo-first-order kinetic model as follows:

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

By integrating both sides, the equation changes as follows:

$$-\ln\left(\frac{C_A}{C_{A0}}\right) = k_{obs}t \tag{2}$$

where k_{obs} is the rate constant of the pseudo-first-order kinetic model, C_{A0} expresses the initial concentration of dye

wastewater, and C_A denotes concentration of dye wastewater at time t. In this work, the decolorization of both two sources of dye wastewater was pseudo-first-order kinetics.

3.1. Decolorization and mineralization of dye wastewater by ozonation process

The decolorization and mineralization of synthesized C.I. DB 199 wastewater by oxidization were conducted in a 2 l ozone contactor with initial dye concentration of 20.0 mg l^{-1}. Flowing 6.0 l min^{-1} of oxygen sources such as pure dry oxygen (99.6%) and air into the ozone generator in duplicate for each test was employed. While using pure oxygen for ozone generation, the absorbance of synthesized dye wastewater at 594 nm declined sharply to less than 0.1% of residual color over the retention time of 2.0 min shown in Fig. 2. The removal efficiency of TOC reached about 60% in 15.0 min of retention time that kept unchanged till 40.0 min. Thus, the decolorization of C.I. DB 199 was observed to be a pseudo-first-order kinetic reaction while the rate constants were 2.9980 and 1.2145 min^{-1} by oxygen and air inflow to ozone generator, respectively. The mass transfer coefficients were tested to be 0.0677 and 0.0555 s^{-1} for pure oxygen and air, respectively. Thus, the lower decolorization rate of C.I. DB 199 resulted by air due to lower mass transfer rate. Consequently, mass transfer rate of ozone was the major operating parameter for the decolorization of dye wastewater.

In addition to the ozone mass transfer coefficient, pH was another factor which affected treatment efficiency of dye wastewater by ozonation. The original pH was 4.9, that was adjusted by adding 1.0N NaOH or 1.0N HCl to increase pH to 8.9 and 10.6, or to decrease to 3.3 on the decolorization of synthesized C.I. DB 199 wastewater shown in Fig. 3, while
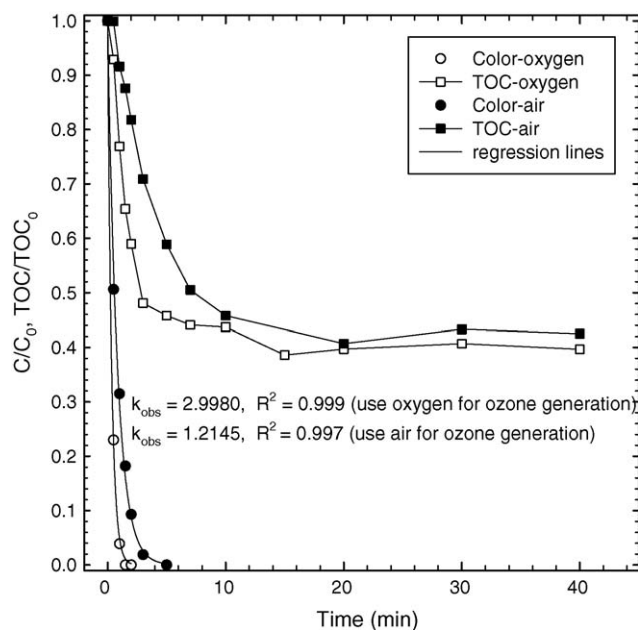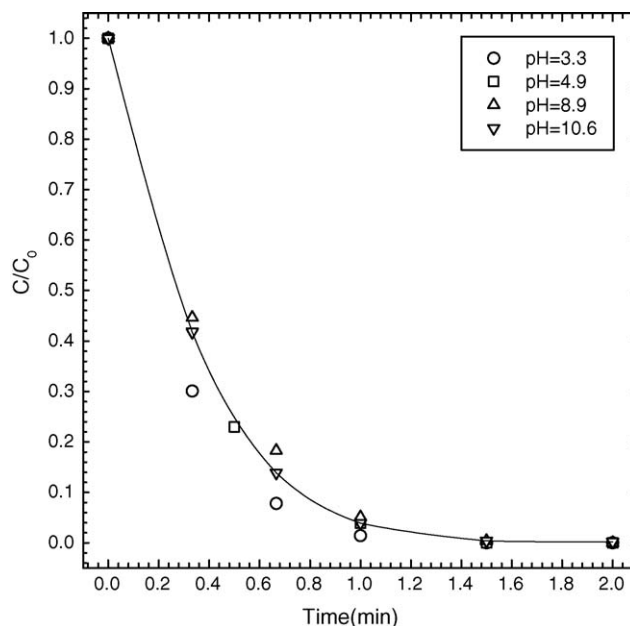

Fig. 3. The normalized concentrations (C/C_0) of C.I. Direct Blue 199 as functions of time in ozonation process under various pHs. The operating conditions were the same as those given in Fig. 2.

the decolorization rate constants were similar no matter what pH. Meanwhile, the TOC reduction was monitored for each test shown in Fig. 4, which expressed TOC versus time under various pH. Accordingly, the TOC removal efficiencies of synthesized dye wastewater were 54%, 60%, 64% and 85% while pH of 3.3, 4.9, 10.6 and 8.9, respectively, over reaction time of 30 min. Although pH did not affect the decolorization rate for C.I. DB 199 wastewater, the mineralization was more efficient at pH 8.9.
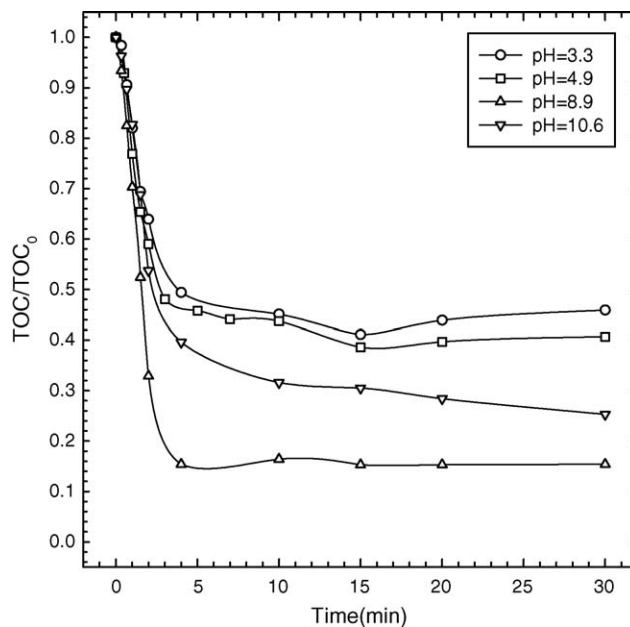

Fig. 2. The normalized concentrations and TOCs (C/C_0 and TOC/TOC$_0$) of C.I. Direct Blue 199 as functions of time in ozonation process with various oxygen sources. Initial dye concentration was 20.0 mg l^{-1} and oxygen (or air) flow rate of 6.0 l min^{-1}. The initial TOC was 6.06 mg l^{-1}.

Fig. 4. The normalized TOCs (TOC/TOC$_0$) of C.I. Direct Blue 199 as functions of time in ozonation process under various pHs. The operating conditions were the same those given in Fig. 2.
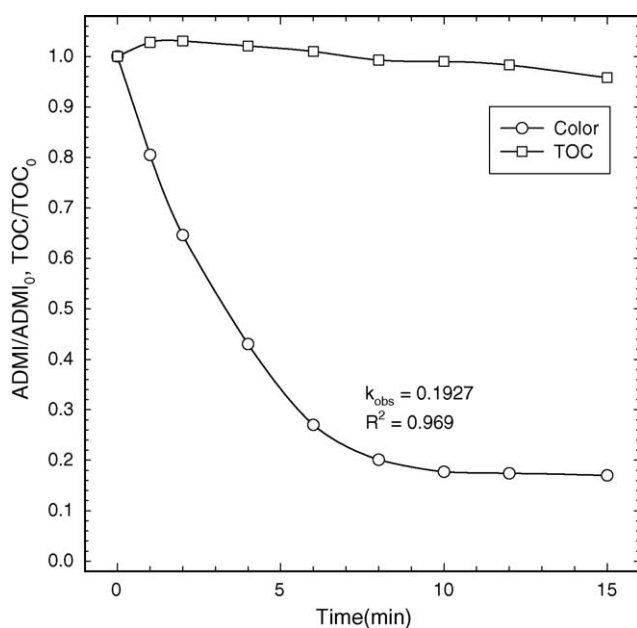
Fig. 5. The normalized color intensities and TOCs (ADMI/ADMI$_0$ and TOC/TOC$_0$) of dye bath effluent as functions of time in ozonation process. The oxygen flow rate to the ozone generator was $6.0 \, l/min^{-1}$. The original TOC was $131.0 \, mg \, l^{-1}$. The color intensity was 780 ADMI units and pH was 6.8.

Fig. 6. The normalized concentrations and TOCs (C/C_0 and TOC/TOC$_0$) of C.I. Direct Blue 199 as functions of time in UV/H$_2$O$_2$ process. The initial hydrogen peroxide concentration was 116.32 mM and UV input power was 560 W. Initial dye concentration was $20.0 \, mg \, l^{-1}$ and the original TOC was $6.06 \, mg \, l^{-1}$.

The dyehouse wastewater containing C.I. DB 199 was more strenuous to be treated than the laboratory synthesized wastewater by ozonation shown in Fig. 5, which indicated over 15 min the decolorization efficiencies reaching 83% and almost 100%, respectively. Thus, $0.1927 \, min^{-1}$ was calculated by the observed pseudo-first order of decolorization for dyehouse wastewater. On the other hand, TOC was employed as an indicator of mineralization while the TOC of dye bath effluent was slightly reduced in 15 min. This implied that the organics of dye bath effluent were so refractory by ozonation that TOC removal obtained as low as 4.0% over 15 min while the original TOC was $131 \, mg \, l^{-1}$. Similar result was reported by Sarasa et al. [14].

3.2. Decolorization and mineralization of dye wastewaters by UV/H$_2$O$_2$ process

The effectiveness of decolorization and mineralization of synthesized C.I. DB 199 wastewater was evaluated by UV/H$_2$O$_2$ process shown in Fig. 6, which plotting the color removal of dye wastewater over time by UV/H$_2$O$_2$ process while the initial dye concentration of $20.0 \, mg \, l^{-1}$, initial hydrogen peroxide concentration of 116.32 mM and UV input power of 560 W. In the process, UV irradiates the H$_2$O$_2$ to produce the strong oxidizing hydroxyl free radicals, which extremely cleave organic bonding promptly. The curve showed that about 90% of color removal was obtained in 30.0 min, which was 0.7 min by ozonation from Fig. 3. The time demand for 90% color removal was about 40 times of variance between two processes. The observed pseudo-first-order rate constant of $0.1673 \, min^{-1}$ by UV/H$_2$O$_2$ process was calculated for synthesized dye wastewater.

In addition, TOC was reduced efficiently by UV/H$_2$O$_2$ process for synthesized C.I. DB 199 wastewater shown in Fig. 6.
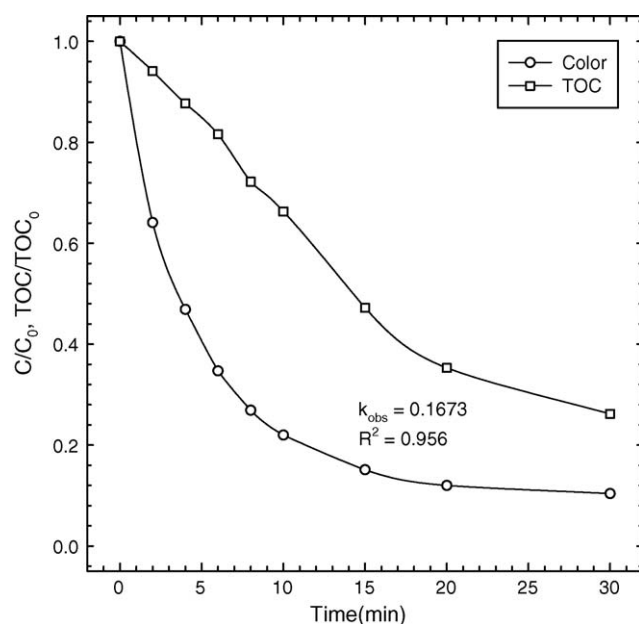
It indicated about 75% of TOC removal over 30.0 min, which expressed the higher mineralization rate than that of ozonation process. It is because of the hydroxyl radicals produced in UV/H$_2$O$_2$ process, which are so strong oxidants as to decompose the organics into smaller molecules. The decomposed intermediates were further converted into carbon dioxide so the TOC was reduced substantially.

The effluents from dye bath usually contain residual colorants or reaction products, dye impurities, auxiliaries and surfactants so that they are more complicate to be decolorized than the laboratory synthesized dye solution. The treatment of dye bath effluent containing C.I. DB 199 by UV/H$_2$O$_2$ process was shown in Fig. 7 while UV intensity of 560 W, initial H$_2$O$_2$ concentration of 116.32 mM and ADMI color intensity of 780 units. From the figure, the time demand for 50% color removal was about 25.0 min, while 3.3 min for synthesized dye wastewater (from Fig. 5). They were about eight times different. The reason for the reduced decolorization by UV/H$_2$O$_2$ process is that some salt ions such as Cl$^-$, SO$_4^{2-}$ and NO$_3^-$ in the dye bath effluent scavenged the hydroxyl free radical, which was also consumed by some organics other than dye molecules or intermediates produced from the reaction itself. This led to decolorization of dye bath effluent more difficult than that of synthesized dye solution while the pseudo-first order decolorizing rate constants of 0.0267 and $0.1673 \, min^{-1}$ obtained for dye bath effluent and the synthesized dye solution, respectively. They were about six times different.

Furthermore, the TOC of dye bath effluent was reduced significantly by UV/H$_2$O$_2$ process, that 87% of TOC removal was reached for the retention time of 120.0 min, which was longer than that of synthesized C.I. DB 199 wastewater. There were some data points higher than 1.0 TOC/TOC$_0$ in Fig. 7 in the first
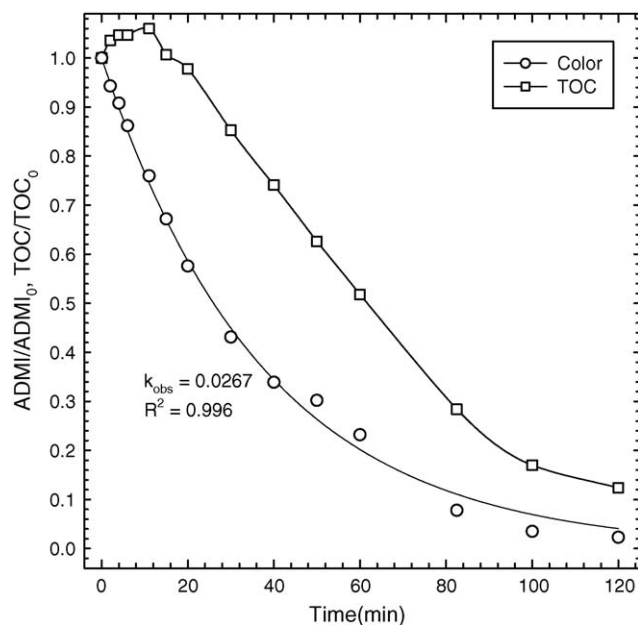
Fig. 7. The normalized color intensities and TOCs (ADMI/ADMI$_0$ and TOC/TOC$_0$) of dye bath effluent as functions of time in UV/H$_2$O$_2$ process. The initial hydrogen peroxide concentration was 116.32 mM and UV input power was 560 W. The wastewater qualities were the same as those given in Fig. 5.

15.0 min because the wet oxidation type TOC analyzer used in this work was without catalyst to convert organic carbon into carbon dioxide. Thus, some refractory organics cannot be detected until the free radical produced from UV/H$_2$O$_2$ process attacked and cleaved them into low molecular organics, which were substantially convertible to be detected by TOC analyzer.

3.3. Decolorization and mineralization of dye bath effluent by sequence ozonation with UV/H$_2$O$_2$ process

From the above results it is clear that ozonation contributed more to the decolorization while UV/H$_2$O$_2$ more to the mineralization of the dye bath effluent. Therefore, the combination of the two processes was expected to provide higher efficiencies of decolorization and mineralization. This is described in the present study. Additionally, the most important disadvantage of UV/H$_2$O$_2$ process in dye wastewater was extremely high absorption of UV light by dye molecules so that the production of hydroxyl radicals was blocked. Thus, ozonation process was considerably designed prior to the UV/H$_2$O$_2$ process for efficient decolorization first. Although effective TOC removal cannot be obtained by ozonation, yet UV/H$_2$O$_2$ process can. Thus, a sequence process by ozonation with UV/H$_2$O$_2$ process was proposed to expect for removing color first by ozonation so that the remaining TOC was reduced by UV/H$_2$O$_2$ process. Thus, a sequence process was proposed by ozonation to remove 85% color in 15.0 min, followed by UV/H$_2$O$_2$ process. In Fig. 8, the time courses of normalized color and TOC (C/C_0 and TOC/TOC$_0$) of dye bath effluent under original pH of 6.8 and the other adjusted pH of 8.9 by sequence ozonation with UV/H$_2$O$_2$ process were presented. There was more than 90% of TOC and color removal within 118.0 and 35.0 min, respectively.
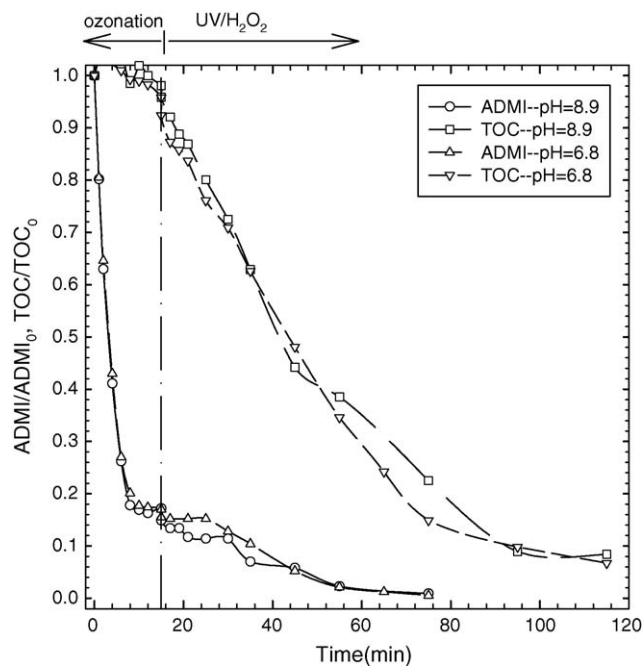

Fig. 8. The normalized color intensities and TOCs (ADMI/ADMI$_0$ and TOC/TOC$_0$) of dye bath effluent as functions of time in sequence ozonation–UV/H$_2$O$_2$ process. The ozonation time was set as 15.0 min then the wastewater was transferred to UV/H$_2$O$_2$ process for further reaction. The initial hydrogen peroxide concentration was 116.32 mM and UV input power was 560 W. The wastewater qualities were the same as those given in Fig. 5.

Also, no significant difference of color and TOC removal was found between pH 6.8 and 8.9.

In order to compare the merit of color removal by sequence ozonation with UV/H$_2$O$_2$ process with UV/H$_2$O$_2$ process alone, the time courses of normalized color intensity were shown in Fig. 9. The sequence process provided the ADMI color
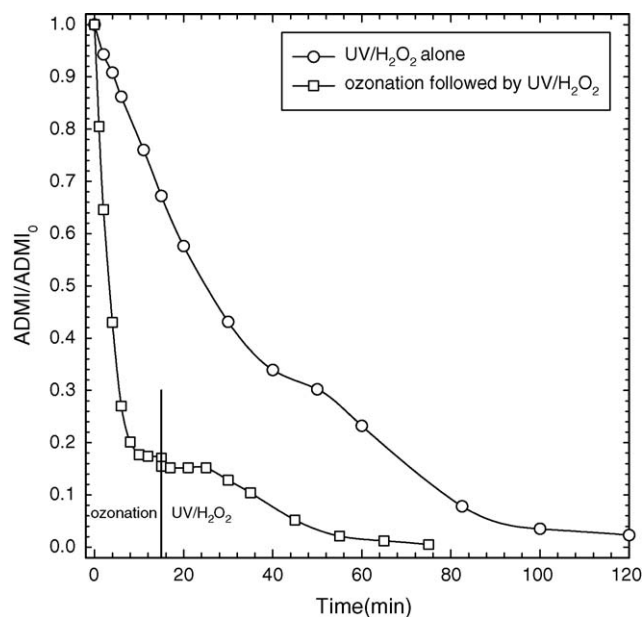

Fig. 9. The comparison of dye bath effluent decolorization by UV/H$_2$O$_2$ process with sequence ozonation–UV/H$_2$O$_2$ process. The wastewater qualities were the same as those given in Fig. 5.

Table 1
Rate constants and half-life decolorization of dye bath effluent and synthesized dye wastewater in various processes

Process	Dye bath effluent			Synthesized dye wastewater		
	k_{obs} (min^{-1})	R^2	$t_{1/2}$ (min)	k_{obs} (min^{-1})	R^2	$t_{1/2}$ (min)
Ozonation	2.998	0.999	0.23	0.1927	0.969	3.6
UV/H$_2$O$_2$	0.1673	0.956	4.1	0.0267	0.996	25.8
Sequence ozonation–UV/H$_2$O$_2$	–	–	–	0.1747	0.919	4.0

reduction sharply about 15% remaining in the beginning 15.0 min by ozonation. Following, the wastewater flowed into the UV/H$_2$O$_2$ reactor that the color was slowly reduced to less than 1.0% remaining within the total time of 75.0 min. On the other hand, for UV/H$_2$O$_2$ process alone, only 33.0% of color removal at first 15.0 min was reached that 98% of color removal demanded 120.0 min. Therefore, the sequence process performed more effective than UV/H$_2$O$_2$ process alone to decrease color as well as TOC.

The first order rate constants and half-life of decolorization were summarized for the various oxidation processes in Table 1. The pseudo-first-order rate constants on decolorization of dye bath effluent and synthesized dye wastewater were acquired as 0.1927 and 2.9980 min^{-1}, respectively, so that they were about 15.6 times of variation by ozonation. Similarly, they were 0.0267 and 0.1673 min^{-1}, respectively, so that there was about 6.3 times of variation by UV/H$_2$O$_2$ process. The half-life of decolorization by ozonation and UV/H$_2$O$_2$ process were 3.6 and 25.8 min, respectively, for dye bath effluent treatment.

4. Conclusions

The dye bath effluent from cotton textile industry and synthesized C.I. DB 199 wastewater were investigated to effectively decolorize by ozonation, UV/H$_2$O$_2$ process, and in sequence ozonation with UV/H$_2$O$_2$ process while the decolorization rates of dye bath effluent and synthesized dye wastewater were determined. The results showed that the three oxidation processes are feasible pretreatment methods for complete decolorization of dye wastewater from textile industries. Additionally, the dye bath effluent was more difficult to be decolorized than synthesized dye wastewater because of complex composition. For dye bath effluent, ozonation can reduce color very fast, but only reaches 83% of color reduction and became slight yellow at the end, though that the TOC was reduced hardly to obtain 4.0% of removal efficiency. Reversely, UV/H$_2$O$_2$ process and sequence process can eliminate TOC thoroughly so that sequence process performed 99% of color reduction and 92% of TOC removal. The pseudo-first-order rate constant on decolorizing was about 6.3 times between dye bath effluent and synthesized dye wastewater by UV/H$_2$O$_2$ process. Furthermore, 90% of decolorization and mineralization of dye bath effluent can be achieved within 30.0 and 95.0 min, respectively by sequence process.

While the results discussed for the comparison DB 199 with dye bath effluent, the color removal was rapidly within 5 and

15 min to obtain almost 100% and greater than 80% by ozonation alone. At the same time period, it provided about 60% and almost no reduction of the TOC, respectively due to incomplete mineralization. However, by UV/H$_2$O$_2$ alone, it consumed longer time for color removal than ozonation to reach only about 80% and 95% in 30 and 120 min, respectively. For TOC removal, it was more efficient than ozonation that about 30% and 80% in 30 and 120 min, respectively. As a result, combination with the above two processes was proposed to enhance not only time-demanding but also the effective removal efficiencies of both color and TOC. The ozonation was employed firstly to effectively remove color rapidly, following by UV/H$_2$O$_2$ process in order to remove TOC efficiently.

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