Pre-ozonation coupled with UV/H$_2$O$_2$ process for the decolorization and mineralization of cotton dyeing effluent and synthesized C.I. Direct Black 22 wastewater

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Abstract

The decolorization and mineralization of cotton dyeing effluent containing C.I. Acid Black 22 as well as synthesized C.I. Acid Black 22 wastewater by means of advanced oxidation processes (AOPs), such as UV/H$_2$O$_2$, O$_3$ and pre-ozonation coupled with UV/H$_2$O$_2$ processes, were evaluated in this study. It was observed that the UV/H$_2$O$_2$ process took longer retention time than ozonation for color removal of dye bath effluent. Reversely, the total organic carbon (TOC) removal showed different phenomena that ozonation and UV/H$_2$O$_2$ process obtained 33 and 90% of removal efficiency for 160 min of retention time, respectively. Additionally, laboratory synthesized dye wastewater was substantially more efficient in the decolorization process than dye bath effluent. Therefore, in this work, pre-ozonation coupled with UV/H$_2$O$_2$ process was employed to enhance the reduction of both color and TOC in dye bath effluent at the same time. At the same time, the retention time demand was reduced to less than 115 min for 90% removal of TOC and color by this combined process.
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Keywords: Advanced oxidation processes (AOPs); Pre-ozonation; Direct Black 22; Dye bath; Decolorization; Mineralization; TOC

1. Introduction

Effluents discharged from textile dyeing and finishing industries are categorized as the most difficult to be disposed by biological, chemical and physical technologies. Those effluents from textile industries are generally high in organic contents and strong color, as well as contain surfactants and additives so that they are non-biodegradable as well as not meeting the effluent standards by traditional activated sludge treatment to result into the serious environmental contamination. Thus, the decolorization technologies become major challenges as well as of increasing importance.

Some studies have shown that textile effluents are very refractory to be biodegraded under aerobic conditions [1,2] because of low BOD/COD ratio. Usually, the conventional treatment methods such as coagulation, activated carbon adsorption, and membrane filtration [3–6] can decolorize the dye wastewater. Nevertheless, they mainly transfer the pollutants from water to solid phase or concentrate liquid solution, which cannot destruct pollutants and need further disposal as well as increasing the treatment cost as well.

Advanced oxidation processes (AOPs), such as ozonation, UV/H$_2$O$_2$, UV/O$_3$, Fe^{2+}/H$_2$O$_2$ and UV/O$_3$/H$_2$O$_2$ are widely used to decompose organic products in industrial wastewater and groundwater. The extensive literature of these technologies have been reviewed by Venkatadri and Peters [7]. These processes have the potential ability to mineralize most of the organic contaminants into carbon dioxide and water. Decolorization of textile effluents and synthesized dye wastewater by AOPs have been investigated by various researchers. Ozonation and ultraviolet induced ozonation were studied by Hafez et al. [8] and Shu and Huang [9] for the successful decomposition of *m*-toluidine azo dye and C.I. Acid Orange 10, respectively. Galindo and Kalt [10] presented that C.I. Acid

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Orange 7 could be decolorized in UV/H_2O_2 process with an optimum molar ratio of H_2O_2/dye about 1754. The literature for treatment of various dyes by UV/H_2O_2 processes have also been reported efficiently by Shu et al. [11], Ince [12], Neamtu et al. [13], Cisneros et al. [14], and Mohey El-Dein et al. [15]. Azbar et al. [16] compared COD and color removal of dyeing effluent by various oxidation processes, such as ozonation, UV/H_2O_2, UV/O_3, Fe^{2+}/H_2O_2 and UV/O_3/H_2O_2 processes. They found the combination of ozone, UV and hydrogen peroxide was the most efficient for decolorization and mineralization of textile effluents. Based on the above literature, AOPs are substantially shown to be feasible treatment technologies for decolorization of textile effluents.

There are two major pollution indicators, color and total organic carbon (TOC), which represent the intensities of pollution for textile effluents. Most of AOPs perform excellent efficacy on decolorization of textile effluents, among which the ozonation process shows more potential than that of UV/H_2O_2 processes [17]. However, the removal or destruction of TOC by ozonation was reported to be very difficult that Sarasa et al. [18] showed only 7% TOC removal of a dye manufacturing wastewater during ozonation. The objective of this study was to determine the feasibility of using O_3, UV/H_2O_2 and pre-ozonation coupled with UV/H_2O_2 processes as alternative treatment technologies for textile dyeing effluent. The operating parameters, such as hydrogen peroxide dosage and pH were evaluated. The preliminary study of decolorization of two direct dyes by ozonation and UV/H_2O_2 processes was reported by Huang et al. [19]. To further investigate the decolorization and mineralization of direct dye, the synthesized C.I. Direct Black 22 wastewater was employed to compare with dye bath effluent from textile industry. Removal ratio of color and TOC were used to evaluate the feasible alternatives. Additionally, the pseudo-first order rate constants and the 90% color removal retention time were obtained to identify the best selection of treatment process for textile dyeing effluents.

2. Experimental

2.1. Material

Hydrogen peroxide was bought from Fluka Chemical (35%, w/w). The azo dye, C.I. Direct Black 22 ($C_{44}H_{32}N_{13}Na_3O_{11}S_3$, molecular weight 1083.99, characteristic wavelength 481 nm) was obtained from Lyntech Industries Inc., Lyndhurst, New Jersey, and used without further purification. Wastewater, which employed in this study from a local textile industry company, was collected from dye bath effluent of a cotton fiber dyeing process with TOC of 295 mg l^{-1}, ADMI color of 1368 units, adsorbance at 481 nm of 0.725 and pH of 6.4. The chemical structure of C.I. Direct Black 22 is shown in Fig. 1. Ozone was generated from Welback T-816 ozone generator in 5% concentration.
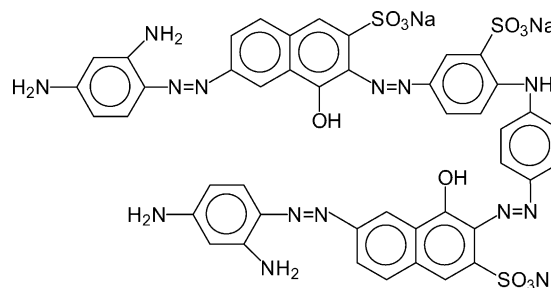

Fig. 1. The molecular structure of C.I. Direct Black 22 studied in this work.

2.2. Apparatus

The UV/H_2O_2 reactor used in this study was a New England Photochemical Co. Model RPR-100 photochemical reactor, which fitted with 16 of RPR-1849/2537Å low pressure mercury arc UV lamps (wavelength 253.7 nm, 35 W per lamp) along the inner wall of reactor. This allowed a total of 560 W that may be applied in a 500 ml quartz stirred vessel. The detail description of reactor configuration can be obtained from our previous paper [20]. Samples were withdrawn at time intervals and analyzed by the spectrophotometer and TOC analyzer. The ozone experiments were conducted in an ozonation reactor designed to perform good mass transfer of ozone throughout wastewater. The reactor vessel was a cylindrical type reactor with 2.4 l holdup volume and operated at 2.0 l capacity (i.d. of 110 mm, height of 250 mm). The bottom of the reactor was equipped with two gas diffusers to produce fine ozone bubbles, which was produced by flowing 6 l min^{-1} high purity oxygen of 99.5% into ozone generator.

2.3. Analyses

Optical absorption spectrum of C.I. Direct Black 22 was determined by a Varian DMS 200 Visible–UV spectrophotometer. The wavelength of maximum adsorption for C.I. Direct Black 22 was selected for quantitative analysis. The concentration of the synthesized azo dye wastewater containing C.I. Direct Black 22 was measured by the wavelength absorbance at 481 nm. The absolute concentration of dyes in the cotton dyeing effluent could not be determined through single wavelength absorbance that the standard color detection procedure developed by the American Dye Manufacturers Institute (ADMI) recommended. ADMI color value 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 applied in this study was described in method 2120E of Standard Methods [21]. The absorbance values of 30 wavelengths were identified by spectrophotometer. An IO Analytical 700 TOC analyzer was employed to detect the TOC of wastewater, which was utilized to estimate the mineralization of dissolved organic compounds. Hydrogen peroxide concentration was

determined by spectrophotometer method proposed by Masschelein et al. [22]. Ozone concentration was measured by iodometric method proposed by Shechter [23].

3. Results and discussion

3.1. Rate expression of pseudo-first order reaction by UV/H₂O₂ and ozonation

From our previous study [20], the rate expressions for the decolorization of azo dyes by UV/H₂O₂ process were summarized in Table 1. Similarly, the decolorization rate can be expressed as Eq. (4) in Table 1 for ozonation of azo dye by assuming excess amount of gas ozone was flowed into liquid phase, the aqueous ozone concentration reached equilibrium instantaneously. Thus, C_{O_3} was treated as a constant.

3.2. Decolorization of synthesized wastewater and dye bath effluent with C.I. Direct Black 22 by UV/H₂O₂ process

The effluents from cotton dyeing bath usually contain unbound colorants or reaction products, dye impurities, auxiliaries and surfactants. Thus, the dye bath effluents are more difficult to be decolorized than laboratory synthesized dye solution. Therefore, the experiment was designed for comparison with the decolorization of synthesized wastewater and dye bath effluent containing C.I. Direct Black 22 by UV/H₂O₂ process for UV intensity of 560 W, initial H₂O₂ concentration of 116.32 mM and initial dye concentration of 20.0 mg l⁻¹ (18.5 μM) shown in Fig. 2. The synthesized dye solution was prepared in similar color intensity to the dye bath effluent, absorbance of 0.725 at 481 nm, so that the results showed effluent from dye bath with C.I. Direct Black 22 was less efficient for decolorization in the process. Obviously, the time demand of 95% color removal was obtained in 7.3 min for synthesized dye solution and 80 min of time demand to reach 58% color removal for dye bath effluent. The ions such as Cl⁻, SO₄²⁻ and NO₃⁻ in the dye bath effluent may act as scavengers in the free radical reactions and the organics other than dye molecules also consume free rad-

Table 1
Rate expressions for UV/H₂O₂ and ozonation employed in this study

Eq. no.	Equations	Remark
(1)	$\frac{dC_A}{dt} = -kC_A C_{OH^\bullet}$ [a]	C_A, the concentration of azo dye; $C_{OH^\bullet}$, the concentration of hydroxyl radical; t, the reaction time
(2)	$\frac{dC_A}{dt} = -k_{obs} C_A$	k_{obs}, the rate constant of the pseudo-first order kinetic model
(3)	$-\ln\left(\frac{C_A}{C_{A_0}}\right) = k_{obs} \times t$	C_{A_0}, the initial concentration of azo dye
(4)	$\frac{dC_A}{dt} = -kC_A C_{O_3}$	C_{O_3}, concentration of aqueous ozone

[a] Assuming the hydroxyl radical concentration reaches equilibrium instantaneously in the presence of excess hydrogen peroxide. Thus, $C_{OH^\bullet}$ is treated as a constant.
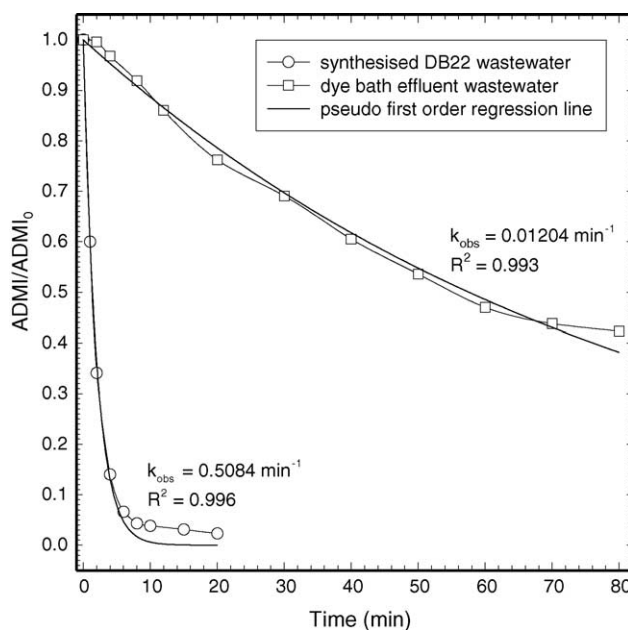

Fig. 2. The normalized color intensities (ADMI/ADMI₀) of dye bath effluent and synthesized dye wastewater as functions of time in UV/H₂O₂ process. Initial dye concentration was 20.0 mg l⁻¹ (18.5 μM) and hydrogen peroxide concentration was 116.32 mM, UV light of 560 W. The ADMI color unit of dye bath effluent was 1368.

icals and be decomposed in the reaction. Therefore, the free radicals used for decolorization are reduced by both scavengers and organics. This explains why the decolorization of dye bath effluent is more difficult than that of synthesized dye solution. Besides, the changes in normalized color intensity (ADMI/ADMI₀) with time for both dye wastewaters were based on the above equations in Section 3.1 that the observed pseudo-first order rate constants of 0.01204 and 0.5084 min⁻¹ were calculated by linear regression, and the square of relative correlative coefficients (R^2) of 0.993 and 0.996 for dye bath effluent and synthesized dye wastewater, respectively.

On the other hand, ratio of residual to initial color intensity of dye bath effluent versus time by various hydrogen peroxide concentrations were plotted in Fig. 3, for UV intensity of 560 W and ADMI color intensity of 1368 units. The hydrogen peroxide concentration was stoichiometricly overdosed and was measured to be relatively unchanged during the experiments. From our previous study [20], there was an optimum ratio of hydrogen peroxide to dye concentration ($C_{H_2O_2}/C_{dye}$) of about 500/800 for C.I. Acid Black 1. Similarly, the observations of optimal $C_{H_2O_2}/C_{dye}$ also were observed to be 851 and 826–1100 by Cisneros et al. [14] and Ince [12] for azo dyes Hispamin Black CA and Remazol Black-B, respectively. Indeed, the complicate composition in the wastewater of dye bath effluent results into the difficulty to determine the initial dye concentration. Accordingly, the higher hydrogen peroxide doses from 29.08 to 232.64 mM were employed for decolorization of the dye bath effluent that the decolorization rate increased significantly by incre-
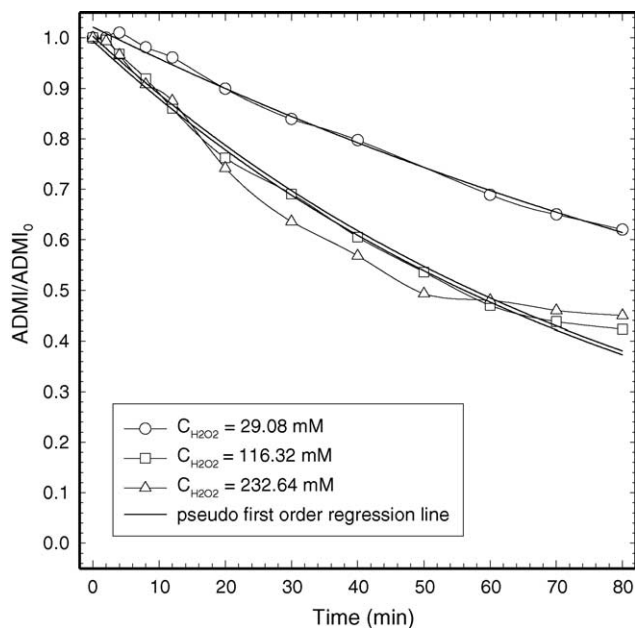
Fig. 3. The normalized color intensities (ADMI/ADMI$_0$) of dye bath effluent as functions of time in UV/H$_2$O$_2$ process with various hydrogen peroxide concentrations. Initial color intensity was 1368 ADMI units and hydrogen peroxide concentration varied from 29.08 to 232.64 mM at UV light of 560 W.
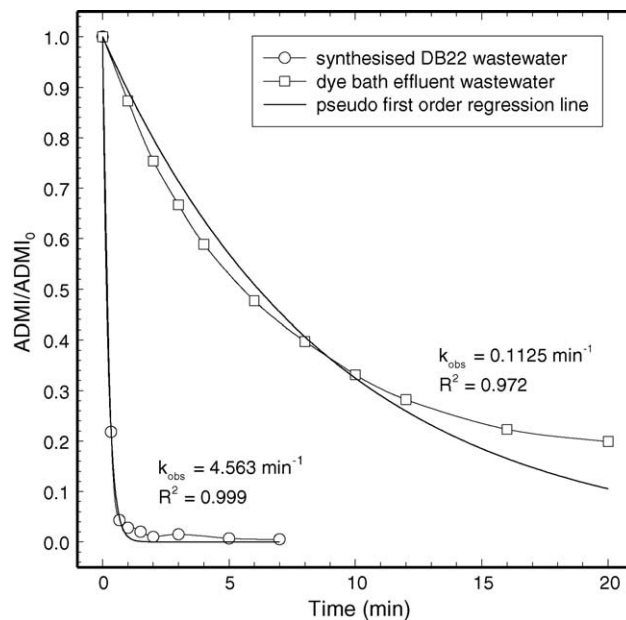

Fig. 4. The normalized color intensities (ADMI/ADMI$_0$) of dye bath effluent and synthesized dye wastewater as functions of time in ozonation process. Initial dye concentration was 20.0 mg l^{-1} (18.5 μM) and oxygen flow rate was 6 l min^{-1} into the ozone generator. The ozone generator condition was set at 110 W and 105 V. The ADMI color unit of dye bath effluent was 1368.

menting the hydrogen peroxide concentrations from 29.08 to 116.32 mM. Nevertheless, continuously increasing H$_2$O$_2$ concentration to 232.64 mM, the decolorization rate showed no substantial improvement over that of 116.32 mM. This is because that the scavenging of hydroxyl radicals by excess hydrogen peroxide causes this adverse effect of higher hydrogen peroxide dosage since OH$^{\bullet}$ was reacted and competition by both by the excess H$_2$O$_2$ and dye in the solution in the photolysis at the same time. Therefore, 116.32 mM of hydrogen peroxide concentration was observed as the better choice for the effective decolorization. Additionally, the color removal efficiencies of dye bath effluent by UV/H$_2$O$_2$ process were only 31, 53 and 52% for hydrogen peroxide concentration of 29.08, 116.32 and 232.64 mM, respectively, in 60 min. This implies the dye bath effluent is difficult to be decolorized by UV/H$_2$O$_2$ process.

3.3. Ozonation of synthesized wastewater and dye bath effluent with C.I. Direct Black 22

The decolorization of synthesized wastewater and dye bath effluent containing C.I. Direct Black 22 were conducted in an ozone contactor of 2 l supplied by initial dye concentration of 20.0 mg l^{-1} (18.5 μM) and an oxygen flow rate of 6.0 l min^{-1} to produce ozone shown in Fig. 4, which follows pseudo-first order reaction. Furthermore, the reaction spontaneously released the organic and inorganic acids so as to decrease pH from 4.9 to 3.6 for retention time of 5 min and the dye concentration declined from 20.0 to less than 0.1 mg l^{-1}. Accordingly, results showed the same situation in UV/H$_2$O$_2$

process that dye effluent from dye bath was more challenging to be decolorized by ozonation while taking 20 min to reach 80% of color removal. By using the same linear regression technique, observed pseudo-first order rate constants of 0.1125 and 4.563 min^{-1} by ozonation are calculated and the square of the relative correlative coefficients (R^2) of experimental data of 0.972 and 0.999 for dye bath effluent and synthesized wastewater, respectively.

pH is one of the major factors which may affect treatment efficiency by ozonation, that the original pH of 6.4 was adjusted by adding 1N NaOH to raise pH to 10.2, or adding 1N HCl to drop off pH to 3.5 on decolorization of dye bath effluent shown in Fig. 5. The decolorization rate constants were about the same for these three pHs. The higher decolorization rate was observed at pH 6.4 without adjustment by NaOH or HCl, which was selected for the decolorization condition of dye bath effluent in the further ozonation experiments. Accordingly, the color removal efficiencies of dye bath effluent by ozonation were 74, 78 and 80% for pH of 3.5, 10.2 and 6.4 for reaction time of 20 min, respectively. The results imply that the dye bath effluent can be decolorized more efficiently by ozonation than that of UV/H$_2$O$_2$ process.

3.4. Mineralization of dye bath effluent by ozonation and UV/H$_2$O$_2$ processes

The effectiveness of mineralization of dye bath effluent was evaluated by two different oxidation processes shown in Fig. 6 that TOC was an indicator of mineralization. The mineralization of wastewater by ozonation is very difficult,
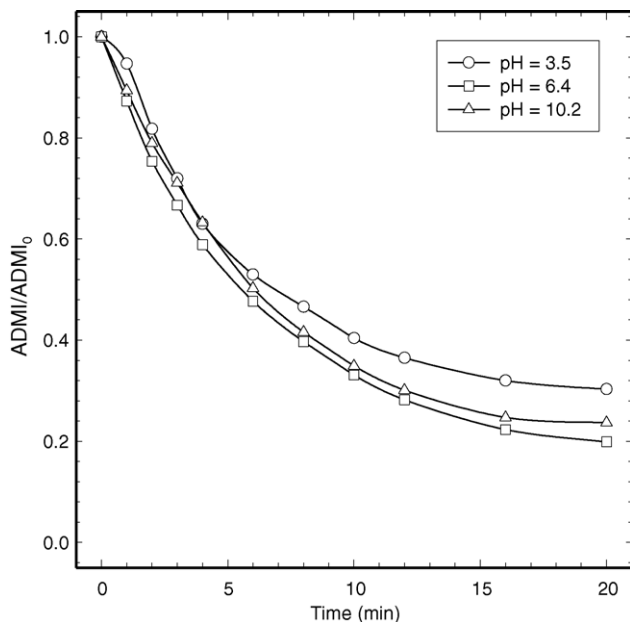
Fig. 5. The normalized color intensities ($ADMI/ADMI_0$) of dye bath effluent as functions of time in ozonation process under various pH. Reaction conditions were the same as those given in Fig. 4.

higher than 1.0 during the first 40 min for UV/H_2O_2 process. Since the TOC analyzer used in this work was a wet oxidation type instrument, it has no catalyst to convert organic carbon into carbon dioxide. Thus, some refractory organics cannot be converted into carbon dioxide properly. In UV/H_2O_2 process, the hydroxyl radicals are powerful oxidants, which can degrade organics into smaller molecules. The decomposed organics are easier to be converted to carbon dioxide and be measured by TOC analyzer. This can explain the higher than

which takes 160 min to obtain as low as 33.2% of TOC removal that the original TOC of dye bath effluent is $295 \, mg \, l^{-1}$ for both processes. Similar result was reported by Sarasa et al. [18]. On the other hand, as high as 91.2% of TOC removal by the UV/H_2O_2 process, which provided higher mineralization rate of dye bath wastewater than ozonation at 160 min of reaction time. It is interesting to observe that TOC/TOC_0 is
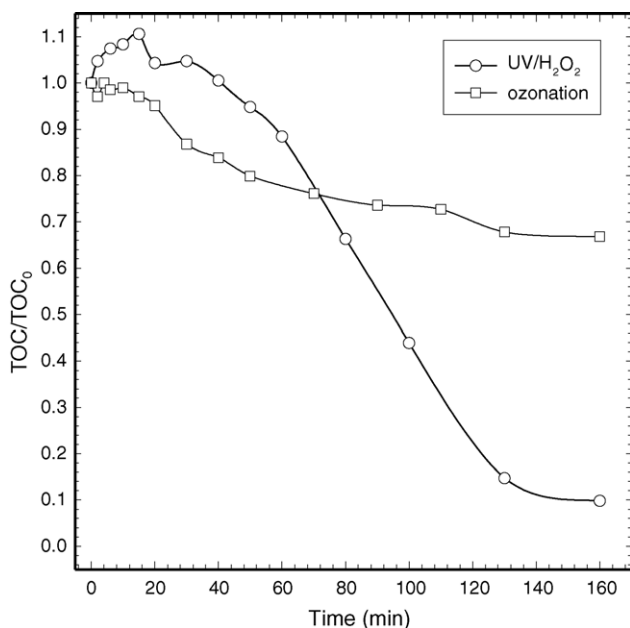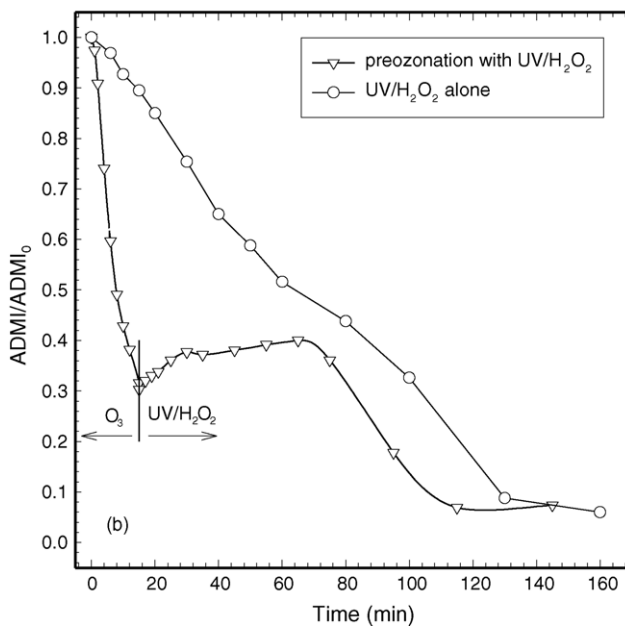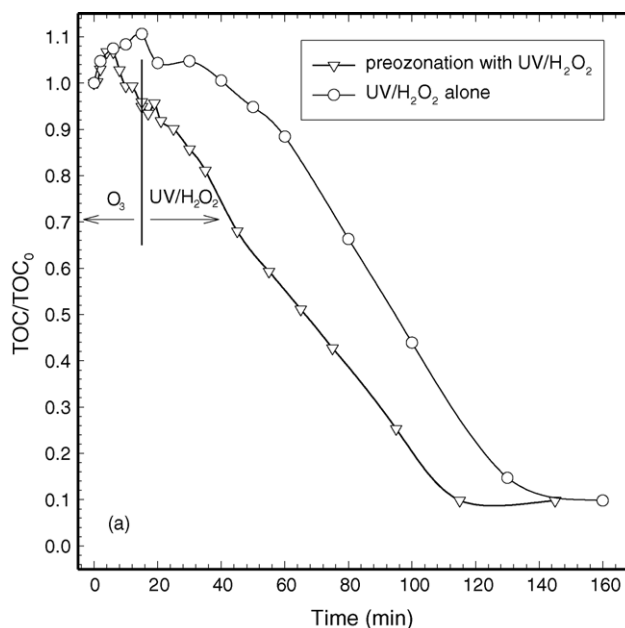

Fig. 6. TOC removal efficiencies vs. time for dye bath effluent in UV/H_2O_2 and ozonation processes. Initial TOC was $295 \, mg \, l^{-1}$. Reaction conditions were the same as those given in Figs. 2 and 4 for UV/H_2O_2 and ozonation, respectively.

Fig. 7. (a) TOC removal efficiencies vs. time, (b) ADMI color removal efficiencies vs. time, for dye bath effluent in UV/H_2O_2 and pre-ozonation with UV/H_2O_2 processes. The pre-ozonation time was 15.0 min. Initial color intensity was 1368 ADMI units and TOC was $295 \, mg \, l^{-1}$. Reaction conditions were the same as those given in Figs. 2 and 4 for UV/H_2O_2 and ozonation, respectively.

Table 2
Rate constants and time demands for 90% color and TOC removal of dye bath effluent and synthesized dye wastewater in various processes

Processes	Dye bath effluent			Synthesized dye wastewater	
	1st order rate constants (min^{-1})	Retention time for 90% color removal (min)	Retention time for 90% TOC removal (min)	1st order rate constants (min^{-1})	Retention time for 90% color removal (min)
UV/H$_2$O$_2$	0.01204	191.2	160.0	0.5084	4.8
Ozonation	0.1125	>20	≫160	4.563	0.5
Pre-ozonation 15 min + UV/H$_2$O$_2$	n.a.	106	115	4.563	0.5
Pre-ozonation 40 min + UV/H$_2$O$_2$	n.a.	70	124	4.563	0.5

n.a., not applicable; combined process by ozanation and UV/H$_2$O$_2$ cannot simply be expressed by single rate constant.

1.0 TOC/TOC$_0$ in Fig. 6. During the reaction, TOC increased from 0 to 20 min and decreased after 20 min of reaction time.

3.5. Pre-ozonation coupled with UV/H$_2$O$_2$ process for decolorization and mineralization of dye bath effluent

From the above results, we knew that the UV/H$_2$O$_2$ process performed better in TOC removal and ozanation resulted into better decolorization. Therefore, the important thought was that improvement in the removal of TOC and color simultaneously can be offered by pre-ozonation in connection with UV/H$_2$O$_2$ process. The idea is trying to use ozanation to remove color first to enhance the free radical formation by higher UV intensity in UV/H$_2$O$_2$ process. Firstly, to remove 70% of color by ozanation, we proposed a combined process with 15.0 min of pre-ozonation followed by UV/H$_2$O$_2$ process. Accordingly, TOC removal of dye bath effluent by UV/H$_2$O$_2$ process with or without 15.0 min of pre-ozonation is shown in Fig. 7a; there was more than 90% of TOC removal within 160 min for both processes. The pre-ozonation coupled with UV/H$_2$O$_2$ process was more effective to decrease TOC than UV/H$_2$O$_2$ process alone. For 90% of TOC removal, pre-ozonation connected with UV/H$_2$O$_2$ process spent about 115 min of reaction time, which was 45 min faster than UV/H$_2$O$_2$ process alone. On the other hand, the results of color removal were shown in Fig. 7b that pre-ozonation provided the ADMI color reduction sharply in the first 15.0 min by ozanation to about 30% of original color intensity. Following, the wastewater was connected into UV/H$_2$O$_2$ process; the color of wastewater was substantially reduced slowly to less than 7% of original color for total reaction time of 115 min. Interestingly, the variation of color during 15–60 min may be caused by the formation of colorful intermediates by UV/H$_2$O$_2$ process. For longer reaction time, the colorful intermediates decomposed substantially.

In the case of UV/H$_2$O$_2$ process without pre-ozonation, the decolorization decelerated with a constant reaction rate while taking 160 min to reach about 94% color removal. Consequently, 15.0 min of pre-ozonation connected with the UV/H$_2$O$_2$ process as a combination oxidation process were capable to effectively remove color and TOC in dye bath effluent, as well as reduce the time demand for 90% removal of color and TOC. The first order rate constants and time de-

mand for 90% of color and TOC removal are summarized for the various oxidation processes in Table 2. The pseudo-first order rate constants on decolorization of dye bath effluent and synthesized dye wastewater were acquired as 0.01204 min^{-1} and 0.5084 min^{-1}, respectively, so that they were about 42 times of variation by UV/H$_2$O$_2$ process. Similarly, they were 0.1125 and 4.563 min^{-1}, respectively, so that there was about 40 times variation by ozanation. The time demand for 90% of color and TOC removal by UV/H$_2$O$_2$ process were 12 and 45 min, respectively, which were longer than by the combination process.

Additionally, to further decolorize to 85% by ozanation, we extended the pre-ozonation time to 40.0 min following connecting UV/H$_2$O$_2$ process in order to furthermore reduce the time demand for 90% color removal shown in Fig. 8. The 90% of color removal can be achieved within 70 min, and the time demand was 124.0 min for 90% of TOC removal which
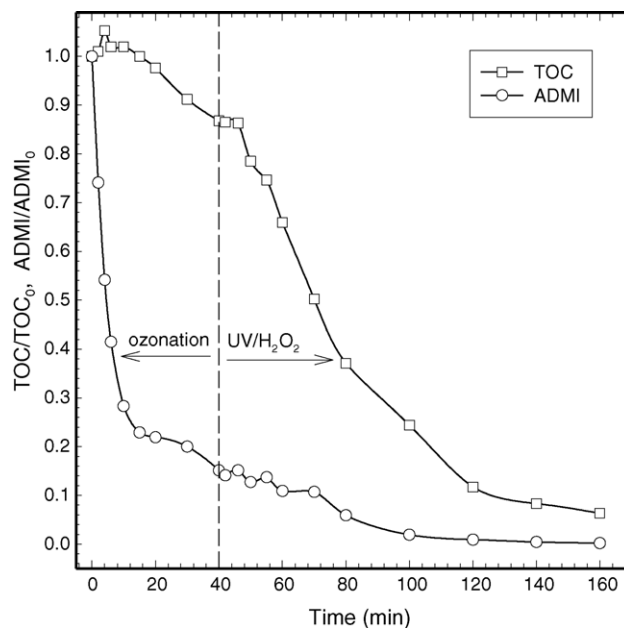

Fig. 8. TOC and ADMI color removal efficiencies vs. time for dye bath effluent in UV/H$_2$O$_2$ and pre-ozonation with UV/H$_2$O$_2$ processes. The pre-ozonation time was 40.0 min. Initial color intensity was 1368 ADMI units and TOC was 295 mg l^{-1}. Reaction conditions were the same as those given in Figs. 2 and 4 for UV/H$_2$O$_2$ and ozanation, respectively.

was 9 min longer compared to the combination process with 15.0 min pre-ozonation.

4. Conclusions

The dye bath effluent from cotton textile industry and synthesized C.I. Direct Black 22 wastewater were investigated to effectively decolorize using the UV/H_2O_2 process, ozonation, and pre-ozonation coupled with UV/H_2O_2. The dye bath effluent was more difficult to be decolorized than synthesized dye wastewater because of its complex composition. For dye bath effluent, ozonation can reduce color very fast, but only reaches 70–83% in color reduction. At the end of ozonation experiment, the treated solution became slight yellow. The TOC in dye bath effluent can only be decomposed slowly and partially, perhaps 33.0%. However, UV/H_2O_2 process and pre-ozonation coupled with UV/H_2O_2 process can eliminate TOC thoroughly that combination process performed 93–99% of color reduction and 91–98% of TOC removal. The pseudo-first order rate constant on decolorizing dye bath effluent was about 42 times less than that of synthesized dye wastewater by UV/H_2O_2 process. It was about 40 times by comparing dye bath effluent with synthesized dye wastewater by ozonation. Furthermore, by using pre-ozonation coupled with UV/H_2O_2 process, 90% of decolorization and mineralization of dye bath effluent can be achieved within 106 and 116 min, respectively. Extending pre-ozonation time of 40 min, the time demand for 90% color removal can be reduced sharply to 70 min. However, the time demand slightly increased to 124 min for 90% TOC removal.

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