

Remedy of dye manufacturing process effluent by UV/H₂O₂ process

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Abstract

The effluent from dye manufacturing industry is more difficult to be treated than laboratory synthesized wastewater according to high variability of composition and color intensity. Thus, this study aimed to propose the method for remedying industrial effluent by UV/H₂O₂ process in a recirculated batch reactor system while considering the effects on hydrogen peroxide dosage, UV power and wastewater intensity for the removal of color and COD. From the experimental results, it was feasibly treated that the distinguished removal of color and COD by increasing the hydrogen peroxide dosage and UV power, but not by the strong intensity of industrial effluent. Therefore, UV/H₂O₂ process of the developed reactor was a positively superior treatment or pre-treatment for dye manufacturing plant effluent to comply the regulated requirements. © 2005 Elsevier B.V. All rights reserved.

Keywords: Dye manufacturing plant effluent; UV/H₂O₂ process; Decolorization; COD; Hydrogen peroxide

1. Introduction

Often the dye effluent of manufacturing industry hardly is compliance with the restrictive color criteria resulting from the ineffective treatment by biological or combination with physical/chemical precipitation process. Thus, the dye industry takes advantage of final polishing step reducing the color of effluent by NaOCl for meeting the requirement so that this chlorination forms byproducts, such as chlorophenols and polychlorinated biphenyls (PCBs) damaging severely the surface water and human health. The abundantly complex feature of dye processing effluent, such as raw materials, intermediates, auxiliary chemicals and some residual dyes, which are not diminished effectively by biological process, generates high color and chemical oxygen demand (COD) resulting into the serious environmental problems. In addition, adsorption and coagulation of chemical and physical methods unnecessarily decolorizes the effluents containing aromatic ring with –SO₃H, which is easily dissolved in water. Yet the generated adsorbed material and final disposal

sedimentary sludge are needed to be further treatment expensively required by law enforcement, in spite of essentially transferring the dye from aqueous to solid waste.

The broad literature review by Venkatadri and Peters [1] stated the chemical oxidation technology by UV/H₂O₂ process, Fenton's reagent and UV/TiO₂, which generates hydroxyl free radicals OH• to enhance the degradation of organics, is widely utilized to remedy wastewater and groundwater. The decomposition of BTEX (Benzene, Toluene, Ethylbenzene, and *p*-xylene) in aqueous solution was conducted efficiently by UV/H₂O₂ process [2].

Accordingly, some researches indicated the synthetic dye wastewater in laboratory by UV/H₂O₂ processes which have proven the significant decolorization. Shu et al. [3] demonstrated the feasible degradation of artificial solutions containing two mono-azo dyes by this process as well as the optimal operating variables for decolorization. Two di-azo dyes, such as C.I. Acid Black 1 and C.I. Acid Blue 113 were also effectively decolorized by UV/H₂O₂ process [4,5]. The successful dye degradation by this process was also reported by previous studies [6,7]. Six vinylsulphone reactive dyes were profitably decolorized using UV/H₂O₂ process by Kurbus et al. [8]. Moreover, the effect of hydrogen peroxide for dye decolorization was substantially found to be identical in

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this process [9,10]. The kinetic study of decolorization and mineralization by UV/H₂O₂ process was accomplished both for mono-azo and reactive azo dyes [11,12].

Though the laboratory study has proven to be efficient for remedying the synthesized dye wastewater by UV/H₂O₂ process, there is scare to apply on dye manufacturing plant effluent.

A few examples, such as dechlorination and decolorization for pulp bleach plant effluent [13] and destruction for cyanide wastewater from thermoelectric power station [14] have treated effectively for plant manufacturing effluent by Advanced Oxidation Processes (AOPs). The effluents from textile plant contained a vinylsulphone dye with C.I. Reactive Black 5 and dye-bath additives were also evaluated the influence of variables by UV/H₂O₂ process [15]. For the treatment of dye manufacturing effluent, the investigation proposed feasibly various oxidation methods, such as Fenton reaction to obtain color and COD removal, enhancement of biodegradability for DSD-acid and H-acid wastewater [16,17]. The powerful treatment by a photo-Fenton process achieving high removal efficiencies, such as 80% of COD and 90% of color in 2 h was found by Kang et al. [18]. The combination of ozonation with coagulation processes reaching 62, 50, 42% of color, COD and TOC removal efficiencies, respectively, stated by Sarasa et al. [19]. The catalytic wet air oxidation (CWAO) with Ce₃Cu₁ composite catalyst was employed beneficially for H-acid wastewater treatment, too [20]. Yet little research discussed for the treatment of dye manufacturing effluent by UV/H₂O₂ process.

Thus, the aim of this study was to evaluate the feasibility of the decolorization and COD removal for dye manufacturing effluent by UV/H₂O₂ process while adjusting the hydrogen peroxide concentration, wastewater strength, and

UV input power as well as computing the reaction rates of decolorization.

2. Experimental

2.1. Materials

Hydrogen peroxide was bought from Fluka Co. with 35% (w/w). The water sample was taken directly from product line of the local dye manufacturing plant effluent (DMPE) prior to mix with other stream or flow to wastewater treatment plant. The initial DMPE composed COD of 5720 mg l⁻¹, PtCo color unit of 49,350, TS of 6545 mg l⁻¹, SS of 275 mg l⁻¹ and pH of 2.8. Thus, 50, 20 and 10% of the field concentration strength of DMPE were obtained while diluting it by DI water into 2, 5 and 10 times. The DMPE effluent analysis data and regulation enforced effluent standards were summarized in Table 1.

2.2. Apparatus

The recirculation batch reactor system, which utilized two thin gap annular UV photo-oxidation reactors in series, was conducted in the experiments. Each annular reactor was fitted with a Sterilight[®] low pressure mercury arc UV lamp (wavelength 253.7 nm, input power of 14 W), which was encapsulated by the inner quartz tube of reactor. The schematic diagram of reactor, which was 2.2 cm of outside diameter of the quartz tube, 3.2 cm of the inside diameter of stainless shell, 0.5 cm of the reactor gap size, 30.0 cm of height, and 127.2 cm³ of holding volume, was shown in Fig. 1. The water recirculation of dye effluent was performed by circulating it from reservoir into the thin gap between quartz tube and outer

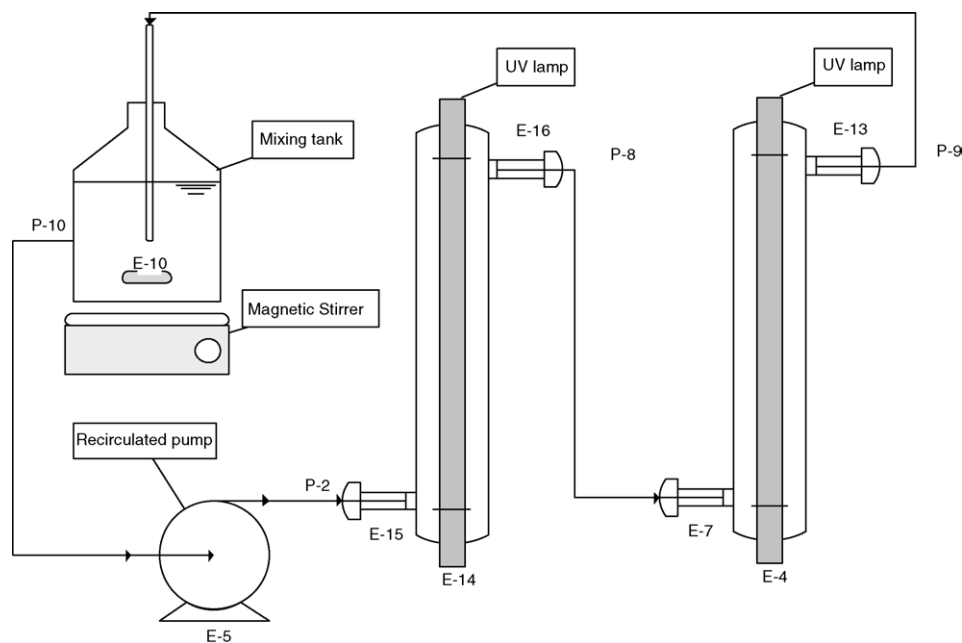


Fig. 1. The schematic drawing of the recirculated batch UV/H₂O₂ process with two annular UV reactors employed.

Table 1
The summary of DMPE effluent characteristics and regulated effluent standards

| | COD (mg l^{-1}) | Color, PtCo unit | TS (mg l^{-1}) | SS (mg l^{-1}) | pH |
|---------------------------------|----------------------------|-------------------------------|---------------------------|---------------------------|---------|
| DMPE effluent analysis | 5720 | 49,350 | 6545 | 275 | 2.8 |
| Effluent standards (Taiwan EPA) | 100 | ADMI 550 ^a (110.4) | NA ^b | 30 | 6.0–9.0 |

^a ADMI is American Dye Manufacturers Institute unit, 550 ADMI is equivalent to 110.4 PtCo unit base on measurements of azo dye, C.I. Acid Blue 24.

^b Not applicable for dye manufacturing industries.

stainless steel shell of reactors one by one, while flowing the outlet effluent from first reactor into the inlet of second reactor, following flowing back to the reservoir and mixing well, again circulating into the annular reactors continuously.

2.3. Analyses

The absolute concentration of DMPE could not be learned by single wavelength absorbance so that the color intensity was detected for measurement of true color using platinum–cobalt (PtCo color unit) Standard Method by Hack[®] DR/2500 Spectrophotometer. Besides, the measurement of COD was using Standard Method 5220C [21]. Thus, the detection ranges for COD of $5720 \pm 130 \text{ mg l}^{-1}$ and PtCo color unit of $49,350 \pm 2600$ were obtained by diluting 2, 5 and 10 times of the original DMPE.

3. Results and discussion

3.1. The effect of hydrogen peroxide concentration on decolorization

Based on previous studies of the authors, the optimal hydrogen peroxide concentration was obtained for the

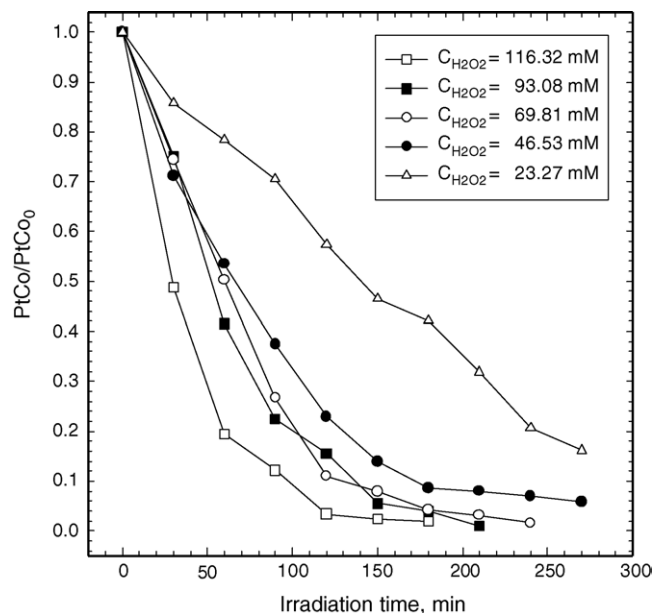


Fig. 2. The fractions of residual PtCo color of dye manufacturing effluent (DMPE) with 10% intensity vs. irradiation time under various hydrogen peroxide concentrations in the UV/H₂O₂ process. The operating condition was under different H₂O₂ initial concentration from 23.27 to 116.35 mM in a 1.01 recirculated batch reactor. UV power input was 28.0 W l⁻¹.

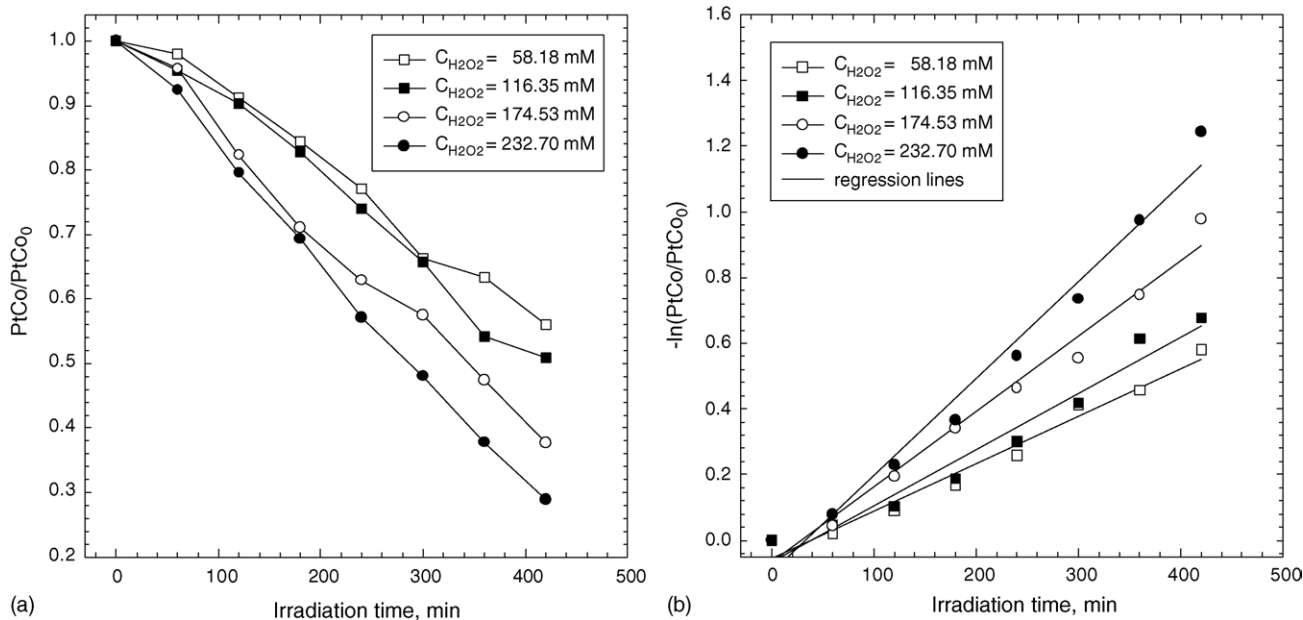


Fig. 3. (a) The fractions of residual PtCo color of DMPE with 50% intensity vs. irradiation time under various hydrogen peroxide concentrations in the UV/H₂O₂ process. (b) The first order rate expression of PtCo color vs. irradiation time as a function of hydrogen peroxide concentration. The operating condition was under different H₂O₂ initial concentration from 58.18 to 232.70 mM in a 1.01 recirculated batch reactor. UV power input was 28.0 W l⁻¹.

dye decolorization of various dyes in laboratory scale by UV/H₂O₂ process. Although, the higher initial hydrogen peroxide concentration, the greater decomposition rate of target compound was observed theoretically. Yet, the progressive OH• free radicals produce till reaching equilibrium, after that it's no more addition in spite of increasing concentration of hydrogen peroxide resulting into ineffective decolorization [4,9,10]. In the other hand, the pollution intensity of DMPE is more complex than that of the laboratory made dye wastewater so that it is refractory for the free radical oxidation resulting into the ineffective treatment in this work. The total solid (TS) and suspended solid (SS) for DMPE were 6545 and 275 mg l⁻¹, respectively, which were high enough to inhibit the decolorization by UV/H₂O₂ process. Essentially, the SS caused UV scattering and dissolved solid (DS) contained free radical scavenging anions, such as Cl⁻, SO₄²⁻, PO₄³⁻, NO₃⁻, etc. The 10% of diluted DMPE was oxidized for decolorization by the UV/H₂O₂ process effectively while hydrogen peroxide of 23.27–116.35 mM shown in Fig. 2. In this experimental condition, the decolorization effect increased by incrementing hydrogen peroxide concentration. For example, in 180 min of reaction time, 57.8, 91.3, 95.8, 96.0 and 98.1% of decolorization were achieved while hydrogen peroxide of 23.27, 46.53, 69.81, 93.08 and 116.35 mM, respectively. In spite the best decolorization effect has not occurred even by the highest concentration of hydrogen peroxide.

If the strength diluted wastewater was raised to 50%, the similar scenario was observed in Fig. 3(a). Though it spent higher dosage of hydrogen peroxide and longer retention time, the less decolorization efficiency was reached than that of 10% diluted dye effluent. For example, in 420 min of retention time, only 44.1, 49.1, 62.3, and 71.1% of decolorization

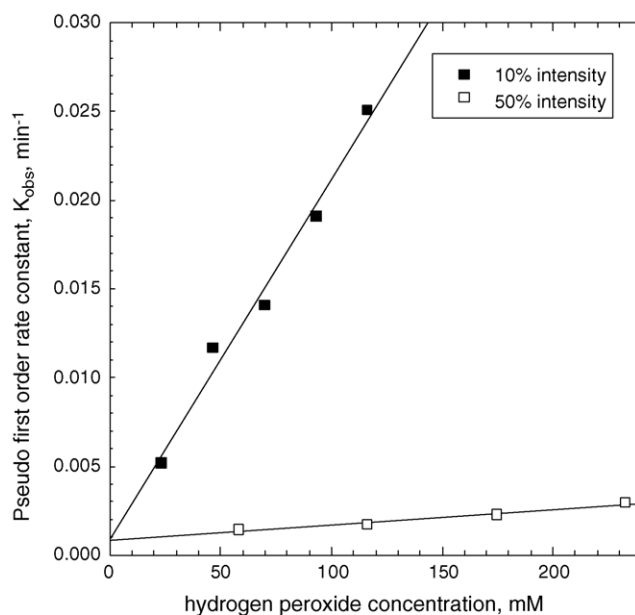


Fig. 4. The pseudo-first order rate constants vs. hydrogen peroxide concentration for various wastewater intensities. The operating conditions were the same as those given in Figs. 2 and 3.

were performed while hydrogen peroxide of 58.18, 116.35, 174.53 and 232.70 mM, respectively. Shu et al. [3,5] investigated the decolorization of dyes by UV/H₂O₂ process that the optimal H₂O₂ dose of 9.8 and 46.53 mM for C.I. Acid Red 1 of 23.56 μM and C.I. Acid Blue 113 of 29.30 μM, respectively. Neamtu et al. [12] also reported an optimal dose of 24.5 mM of H₂O₂ for Disperse Red 354 of 45.76 μM. Indeed in this study, the H₂O₂ concentrations of 116.35 mM and 232.70

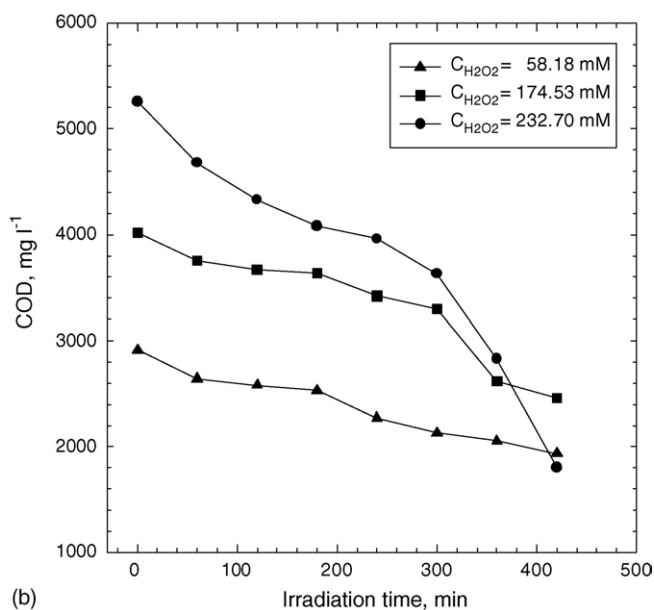
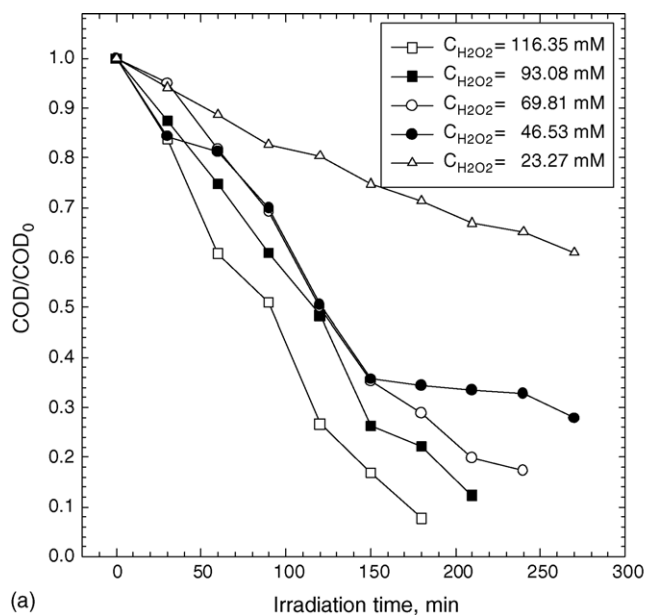


Fig. 5. The fractions of residual COD of DMPE with: (a) 10% (b) 50% intensity vs. irradiation time under various hydrogen peroxide concentrations in the UV/H₂O₂ process. The operating conditions were the same as those given in Figs. 2 and 3.

utilized in 10 and 50% of diluted DMPE were much higher than that of stated above, yet they were still far from the optimum concentration for decolorizing the DMPE. Besides, a pseudo-first order model of DMPE for decolorization was developed as below:

$$\frac{C}{C_0} = e^{-k_{\text{obs}}t} \quad (1)$$

$$-\ln\left(\frac{C}{C_0}\right) = k_{\text{obs}}t \quad (2)$$

where k_{obs} denotes the observed first order reaction rate constant, t expresses the reaction time, C_0 indicates the initial PtCo color unit of wastewater, and C represents the PtCo color unit of wastewater at any irradiation time t . Thus, the k_{obs} is calculated by linear regression shown in Fig. 3(b) while the logarithmic variation in normalized PtCo color unit (C/C_0) versus irradiation time. For example, the k_{obs} values of reaction were 1.449×10^{-3} and $2.952 \times 10^{-3} \text{ min}^{-1}$ while H_2O_2 concentration of 58.18 and 232.70 mM, respectively. Plus, the squares of relative coefficients (R^2) of

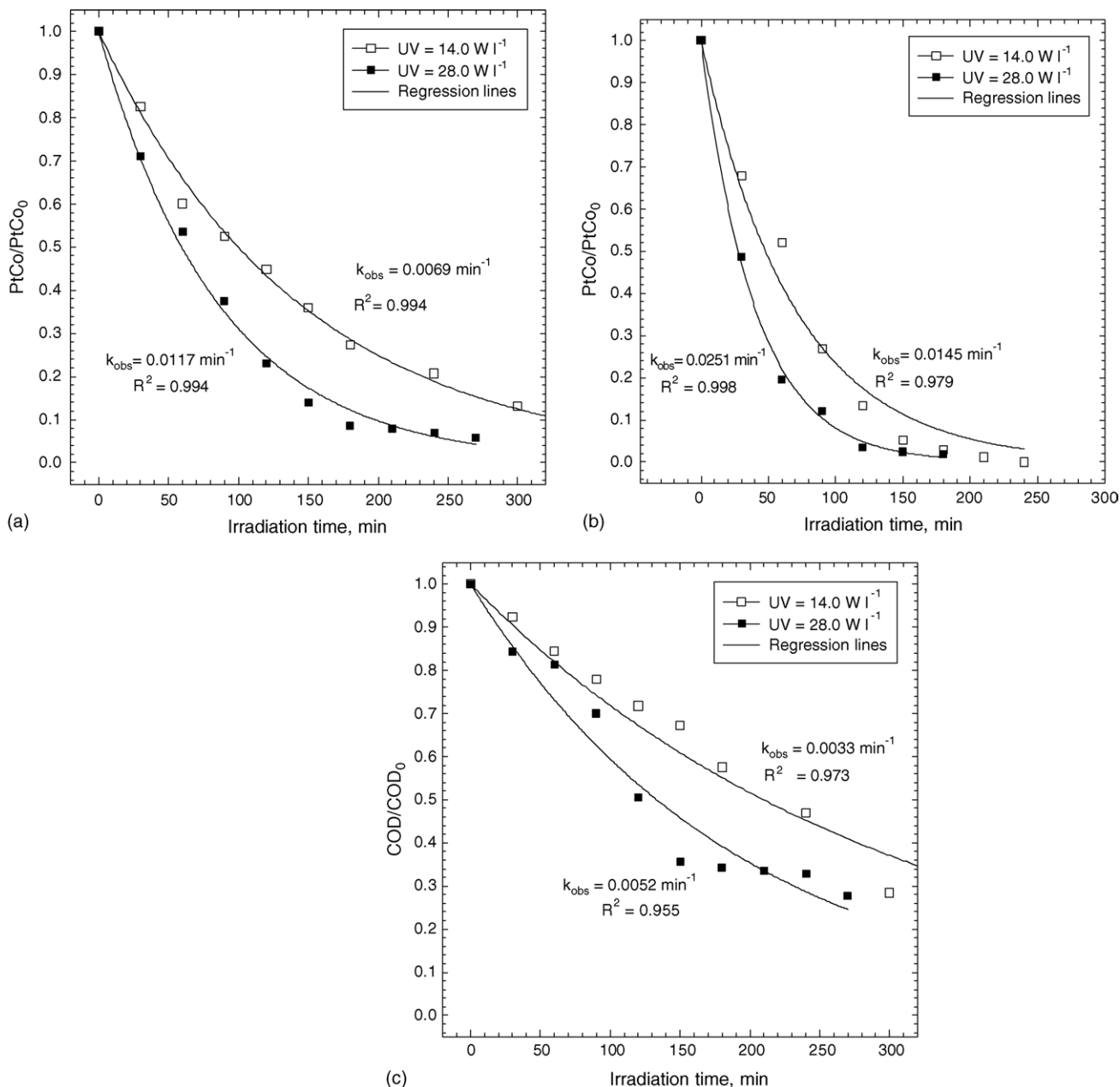


Fig. 6. The fractions of residual PtCo color of DMPE with 10% intensity vs. irradiation time under various UV power inputs in the UV/H₂O₂ process. (a) The hydrogen peroxide concentration was 46.35 mM. (b) The hydrogen peroxide concentration was 116.35 mM. (c) The fractions of residual COD of dye manufacturing effluent with 10% intensity vs. irradiation time under various UV power inputs in the UV/H₂O₂ process for hydrogen peroxide concentration of 46.35 mM. The operating conditions were the same as those given in Figs. 2 and 3.

four tests were calculated about 0.965–0.979 by linear regression.

The relation for k_{obs} and H_2O_2 summarized in Fig. 4 that the k_{obs} increased linearly with respect to incrementing H_2O_2 concentrations. Thus, the above results indicate that the H_2O_2 concentration plays an important role for decolorizing the DMPE in UV/ H_2O_2 process.

3.2. The effect of hydrogen peroxide concentration on COD removal

Except decolorization, the COD disappearance was also affected by H_2O_2 concentration in UV/ H_2O_2 process shown in Fig. 5(a) and (b) for the 10 and 50% of diluted DMPE, respectively. The results indicated that both conditions resulted into very effective COD disappearance of DMPE. The fraction of residual COD (COD/COD_0) versus irradiation time shown in Fig. 5(a), 71.40 and 7.74% of COD residual were achieved by H_2O_2 dosage of 23.27 and 116.35 mM, respectively, in 180 min. The similar trend shown in Fig. 5(b), less COD residual was observed yet it spent longer retention time and higher H_2O_2 dosage. In 420 min, the residual COD of 1800 and 1935 mg l^{-1} was obtained from the initial COD of 2913 and 5260 mg l^{-1} , respectively, while adding 58.18 and 232.71 mM of H_2O_2 dosage. The differences of initial COD for various H_2O_2 dosage cases in Fig. 5(b) were caused by the contribution of COD by H_2O_2 . By UV/ H_2O_2 , COD removal was notably more and more difficult than decolorization by higher and higher strength of DMPE. Interestingly, in Fig. 5(a) for 46.53 mM of H_2O_2 dosage the residual COD remain nearly constant in the time interval of 160 and 240 min, which may be caused by refractory intermediates or final products of UV/ H_2O_2 process. In Fig. 5(b), an important decrease in COD was obtained for 232.7 mM of H_2O_2 dosage after 300 min of treatment. This implies, the COD of organics from DMPE is reduced thoroughly at 300 min of irradiation time and rest of COD is contributed from residual H_2O_2 and can be degraded very sharply.

3.3. The Effect of UV power dosage

The unit UV dosage, a UV power over certain reaction volume as W l^{-1} , was evaluated its effect on decolorization of DMPE shown in Fig. 6(a) and (b) while DMPE intensity of 10% and H_2O_2 concentration of 46.35 and 116.35 mM, respectively. Controlling one or two lamps within the annular reactors perform UV dosages of 14 or 28 W l^{-1} . The higher decolorization rate was obtained by the higher UV lamp power according to the faster formation of OH^\bullet free radical. Thus, the k_{obs} raised by incrementing UV dosage for the same initial H_2O_2 concentration. The amount of UV radiation absorbed by H_2O_2 plays an important role to produce the plentiful OH^\bullet to decolorize the DMPE. In Fig. 6(a), the decolorization followed pseudo-first order reaction that k_{obs} was obtained as 0.0117 and 0.0069 min^{-1} by UV power of 28.0 and 14.0 W l^{-1} , respectively. The rate constant of sin-

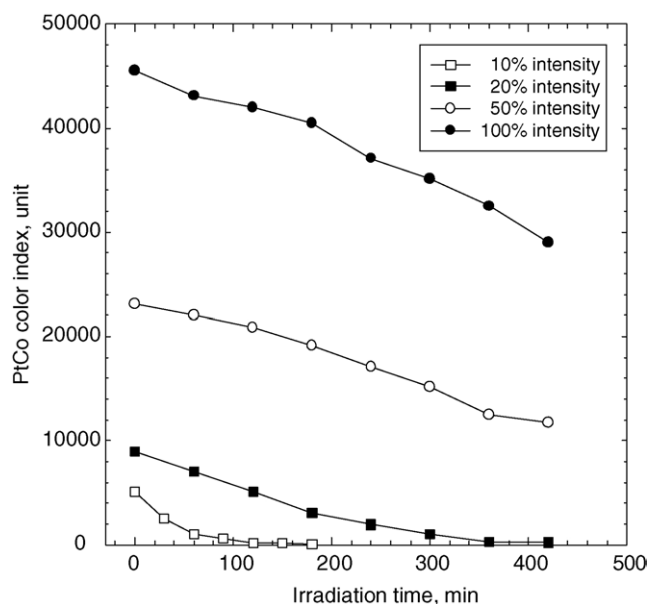


Fig. 7. The residual PtCo color values of DMPE vs. irradiation time under various wastewater intensities in the UV/ H_2O_2 process. The hydrogen peroxide concentration was 116.35 mM and UV power input was 28.0 W l^{-1} .

gle lamp was about 59% of that of twin lamps. Similarly, the k_{obs} of 0.0145 and 0.0251 min^{-1} for UV power of 14.0 and 28.0 W l^{-1} power, respectively, shown in Fig. 6(b). In the other hand, the profile of residual COD fraction versus irradiation time was plotted in Fig. 6(c) under identical conditions as specified for Fig. 6(a). The COD disappearance trends fairly similar to decolorization stated above, however, it is more difficult than color removal for the DMPE treatment.

3.4. Effect of wastewater intensity

The DMPE was diluted with DI water into intensity of 10, 20, 50 and 100%. The effect of DMPE intensity on the decolorization was shown in Fig. 7 plotting the PtCo color unit versus irradiation time, while 116.35 mM of the H_2O_2 concentration and 28.0 W l^{-1} of UV power. From the figure, the lower intensity of DMPE accomplished the better decolorization that almost complete decolorization was observed by 10 and 20% intensity of DMPE. Reversely, for 50 and 100% intensity of DMPE, the PtCo color unit lessened from 23,100 to 11,750 (about 49.1% reduced) and from 45,500 to 29,000 (about 36.3% reduced), respectively, in 420 min. Besides, the COD disappearance with respect to irradiation time by UV/ H_2O_2 process while the various intensity of DMPE was showed in Fig. 8. The lower intensity of DMPE achieved the better COD disappearance so that practically absolute COD disappearance was acquired by 10 and 20% intensity of DMPE. Moreover, over 2000 mg l^{-1} of initial COD, the residual COD approached to 156 and 344 mg l^{-1} within 180 and 420 min, respectively. For 50 and 100% intensity of DMPE, the COD diminished from 3942 to 3159 (20.0% reduced) and from 6820 to 6080 (10.9% reduced) in 420 min, respectively.

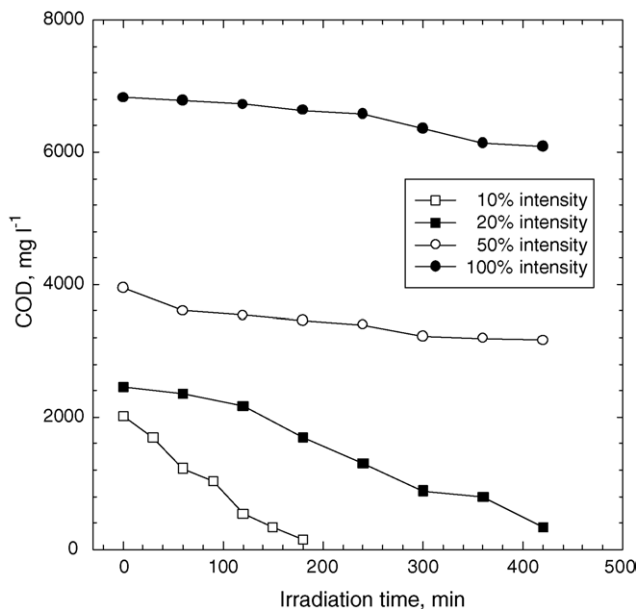


Fig. 8. The residual COD values of DMPE vs. irradiation time under various wastewater intensities in the UV/H₂O₂ process. The operating conditions were the same as those given in Fig. 7.

Consequently, it is observable to find that both PtCo color and COD disappearance efficiency declined significantly by incrementing intensity of DMPE while the H₂O₂ concentration of 116.35 mM and UV dosage of 28.0 W l⁻¹. The result was similar to the observations by other investigators that decolorization rate constants declining by increasing initial dye concentrations.

4. Conclusions

A recirculated reactor system designed for treating color and COD of dye manufacturing plant effluent by UV/H₂O₂ process was proven to be more effective significantly for the lower strength of DMPE while the experimental variables consisted of the hydrogen peroxide dosage, UV power and intensity of DMPE. The rate of decolorization and COD disappearance ascended by raising the H₂O₂ concentration under the certain operating conditions, yet the optimal H₂O₂ concentration was hardly observed. Additionally, incrementing UV power resulted into the increase in color and COD disappearance under various H₂O₂ dosages while the intensity of DMPE caused opposite effect. For 10% intensity of DMPE, the efficiencies of COD and color disappearance of 92.3 and 98.1% were achieved in 180.0 min, respectively. For higher intensity of 50%, the efficiencies of COD and color disappearance reached only 20.0 and 49.1% in 420.0 min, respectively. Consequently, the diluted DMPE with other process water is suggested for the future field application in order to acquire the more efficient treatment effectiveness of COD and color.

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