

Photodegradation of Reactive Black 5, Direct Red 28 and Direct Yellow 12 using UV, UV/H₂O₂ and UV/H₂O₂/Fe²⁺: a comparative study

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Received 23 May 2004; received in revised form 27 July 2004; accepted 17 August 2004

Available online 29 September 2004

Abstract

The photodegradation of three commercially available dyestuffs (C.I. Reactive Black 5, C.I. RB5, C.I. Direct Yellow 12, C.I. DY12, and C.I. Direct Red 28, C.I. DR28) by UV, UV/H₂O₂ and UV/H₂O₂/Fe(II) processes was investigated in a laboratory-scale batch photoreactor equipped with an 16 W immersed-type low-pressure mercury vapour lamp. The experimental results were assessed in terms of absorbance and total organic carbon (TOC) reduction. The initial concentration was kept constant at 100 mg l⁻¹ for all dyes. Initial results showed that, color removal efficiencies by UV or H₂O₂ alone were negligible for all dyes. Almost complete disappearance of C.I. RB5 (99%) and DY12 (98%) in UV/H₂O₂ process was possible to achieve after 60 min of irradiation. The maximum color removal efficiency of C.I. DR28 after 60 min of irradiation, however, was only 40% and reached a maximum value of 70% after 120 min of irradiation. Corresponding mineralization efficiencies were 50, 55 and 7–12%, respectively. The addition of Fe(II) to the system, so-called the photo-Fenton process, greatly enhanced the color removal, the efficiencies being 98, 88 and 85% for C.I. RB5, C.I. DY12 and C.I. DR28 only after 5 min of irradiation. Corresponding mineralization efficiencies were 98% for 45 min irradiation, 100% for 60 min irradiation and 98% for 90 min irradiation, respectively. However, marginal benefit was less significant in the higher range of both H₂O₂ and Fe(II). Furthermore, decreases in both decolorization and mineralization were observed at higher concentrations of oxidant and catalyst due to the scavenging effect of excess H₂O₂ and OH• radicals. The degradation of all dyes was found to follow first-order reaction kinetics.

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Keywords: Decolorization; C.I. Direct Red 28; C.I. Direct Yellow 12; Photodegradation; C.I. Reactive Black 5; UV/H₂O₂/Fe(II)

1. Introduction

The textile industry produces large quantities of highly colored effluents, which are generally toxic and resistant to destruction by biological treatment methods. Most of the dyestuffs used are complexly structured polymers with low biodegradability. They are either sorbed or trapped in bioflocs [1–3]. Thus, ecosystems of streams can be seriously affected if these effluents are not treated properly. Particularly reactive azo dyes cause special environmental concern due to their degradation products such as aromatic amines which

are considered highly carcinogenic [4]. Consequently, dyes have to be removed in dye wastewater before discharge. In the past, effluents containing azo dyes have been treated by adsorption onto activated carbon or by chemical coagulation [5]. However, these traditional methods mainly transfer the contaminants from wastewater to solid wastes.

Advanced oxidation is a potential alternative to decolorize and reduce recalcitrant wastewater loads from textile dyeing and finishing effluents [6]. The research and development in advanced oxidation technologies (AOTs) for water and air remediation have made great progress in recent years, especially the H₂O₂ and TiO₂-based processes. Chemical oxidation using ultraviolet radiation (UV) in the presence of hydrogen peroxide (H₂O₂) is a very promising technique. UV wavelengths of 200–280 nm lead to disassociation of

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H_2O_2 , with mercury lamps emitting at 254 nm being the most commonly used. UV/ H_2O_2 systems generate hydroxyl radicals (OH^\bullet) which are highly powerful oxidizing species. The OH^\bullet yield can be further increased by addition of Fe(II)/(III) species following the pathway of Fenton (Fe(II)/(III)– H_2O_2) and/or photo-Fenton (Fe(II)/(III)– H_2O_2 –UV) reactions. Hydroxyl radicals can oxidize organic compounds (RH) producing organic radicals (R^\bullet) which are highly reactive and can be further oxidized [7,8].

Several dyes utilized by textile industries (including azo-reactive ones) have been successfully degraded by the above techniques [9–15]. Furthermore, though it has been already demonstrated that AOTs can be effectively applied for the degradation of textile dyes in numerous previous studies, many have focused on the color disappearance kinetics. However, it is the ultimate oxidation of TOC content of the dyestuffs that has to be considered for the full-scale applications of AOTs. With the aim to contribute to the clarification of the above mentioned facts, the present study aimed to comparatively evaluate the efficiency of applying UV, UV/ H_2O_2 and UV/ H_2O_2 /Fe(II) processes for photodegradation and also mineralization of three common dyestuffs (C.I. RB5, C.I. DR28, C.I. DY12) which are currently widely used in textile industry.

2. Experimental

2.1. Reagents

C.I. RB5, C.I. DR28, C.I. DY12 are widely used textile dyestuff in the Turkish textile industry and were obtained from far-east as commercially available dyes and used without further purification. Characteristics of the dyes used are listed in Table 1. The H_2O_2 solution (35%, w/w), H_2SO_4 (98–99%) and ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) used as a source of Fe(II) were analytical grade and purchased from Merck. The 1000 mg l^{-1} Fe(II) stock solution was prepared for further dilution to obtain a solution of desired concentration. The pH of aqueous solutions was

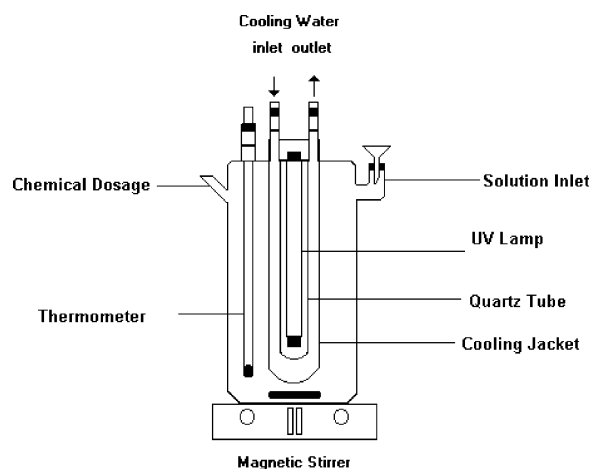


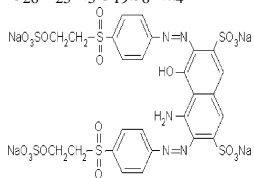
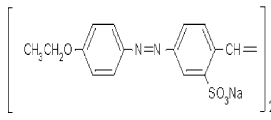
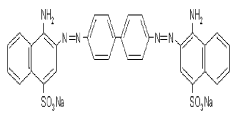
Fig. 1. Schematic diagram of the lab-scale photochemical reactor.

adjusted using sulfuric acid solution when needed. Aqueous solutions of dyestuffs were prepared with distilled water.

2.2. Photoreactor

All experiments were performed in a well stirred, batch, cylindrical photoreactor with a total volume of 2.2 L. The reactor is made of glass and does not contain any metal parts. The outside of the reactor was covered with an aluminium sheet. At the top, the reactor has inlets for feeding reactants, and ports for measuring temperature and withdrawing samples. The reactor was open to air with a Teflon-coated magnetic stirring bar placed at the bottom to provide proper mixing. The UV irradiation source was a 16 W low-pressure mercury vapour lamp (maximum emission at 254 nm) encased in a quartz tube. Because the light source produces heat, the lamp was surrounded with a water-cooling jacket, made of glass, to maintain a constant temperature. The lamp was axially centered and immersed in the dye solution. Fig. 1 illustrates the schematic diagram of the laboratory-scale photochemical installation used in the study.

Table 1
Main characteristics of the dyes used

	C.I. RB5	C.I. DY12	C.I. DR28
Color index no.	20505	24895	22120
Synonyms	Remazol Black B	Chrysophenine yellow	Congo red
Molecular formula	$\text{C}_{26}\text{H}_{25}\text{N}_5\text{O}_{19}\text{S}_6\text{Na}_4$	$\text{C}_{30}\text{H}_{26}\text{N}_4\text{O}_8\text{S}_2\text{Na}_2$	$\text{C}_{32}\text{H}_{24}\text{N}_6\text{O}_6\text{S}_2\text{Na}_2$
Chemical structure			
Molecular weight (g mol^{-1})	991.82	680.70	696.67
λ_{max} (nm)	597	405	497
Purity (%)	~55	~65	~85

2.3. Experimental procedure and analytical methods

For a standard reaction run, 2L aqueous solution of 100 mg l^{-1} dye concentration was used. Experiments with UV and UV/ H_2O_2 were conducted at pH 7 without buffering. Following the adjustment of dyestuff concentration in the solution and pH, it was poured into the reactor. Then, hydrogen peroxide of a desired amount was injected in the reactor before the beginning of each run for UV/ H_2O_2 process. For the photo-Fenton process (UV/ $\text{H}_2\text{O}_2/\text{Fe(II)}$), the pH value of the solution was set to 3 by adding required amounts of H_2SO_4 solution before a given weight of iron salt was added. The iron salt was mixed very well with the prepared dye solution before the addition of a given volume of H_2O_2 . The time at which the ultraviolet lamp was turned on was considered time zero or the beginning of the experiment which was taking place simultaneously with the addition of hydrogen peroxide. The temperature of the solution was kept constant at $25 \pm 2^\circ\text{C}$ throughout all experiments.

Samples were taken at predetermined time intervals to measure absorbance, TOC and pH. The samples were analyzed immediately to avoid further reaction. A spectrophotometer of Novaspec II (Pharmacia Biotech.) was used to measure the absorbance. Absorbance measurements were performed at the wavelength corresponding to maximum absorbance of each dye given in Table 1. TOC measurements were carried out using a DOHRMAN DC 190 model TOC analyser. pH was measured by using NEL pH 890 pH meter.

3. Results and discussion

3.1. Decolorization studies

Initial results demonstrated that neither H_2O_2 (10 mM, pH 7, data not shown) nor UV alone was able to appreciably decolorize C.I. RB5, C.I. DY12 or C.I. DR28 (100 mg l^{-1}). The combination of UV/ H_2O_2 was, therefore, necessary for the production of OH^\bullet radicals to initiate the decolorization of concerning dyes. In order to observe the effect of oxidant concentration on the rate of degradation of three dyestuffs in UV/ H_2O_2 process, experiments were carried out by varying the dose of H_2O_2 from 1 to 100 mM. The results are illustrated in Fig. 2a–c, respectively. As can be seen from Fig. 2, direct photolysis (in the absence of H_2O_2) of all dyes after 2 h of irradiation was almost negligible, 2, 3 and 1% for C.I. RB5, C.I. DR28 and C.I. DY12, respectively within the limits of accuracy of analysis. The decolorization efficiency, however, was enhanced by the addition of H_2O_2 due to the OH^\bullet radicals generated during photochemical reactions. The results also showed dependence of the decolorizing degree on the initial concentration of the hydrogen peroxide. The resistance to destruction by hydroxyl radicals was, however, different for each dye. It was possible to achieve almost complete decolorization in 60 min for C.I. RB5 (99%) and C.I. DY12 (98%) at H_2O_2 concentrations of 25 and 10 mM, respectively. The

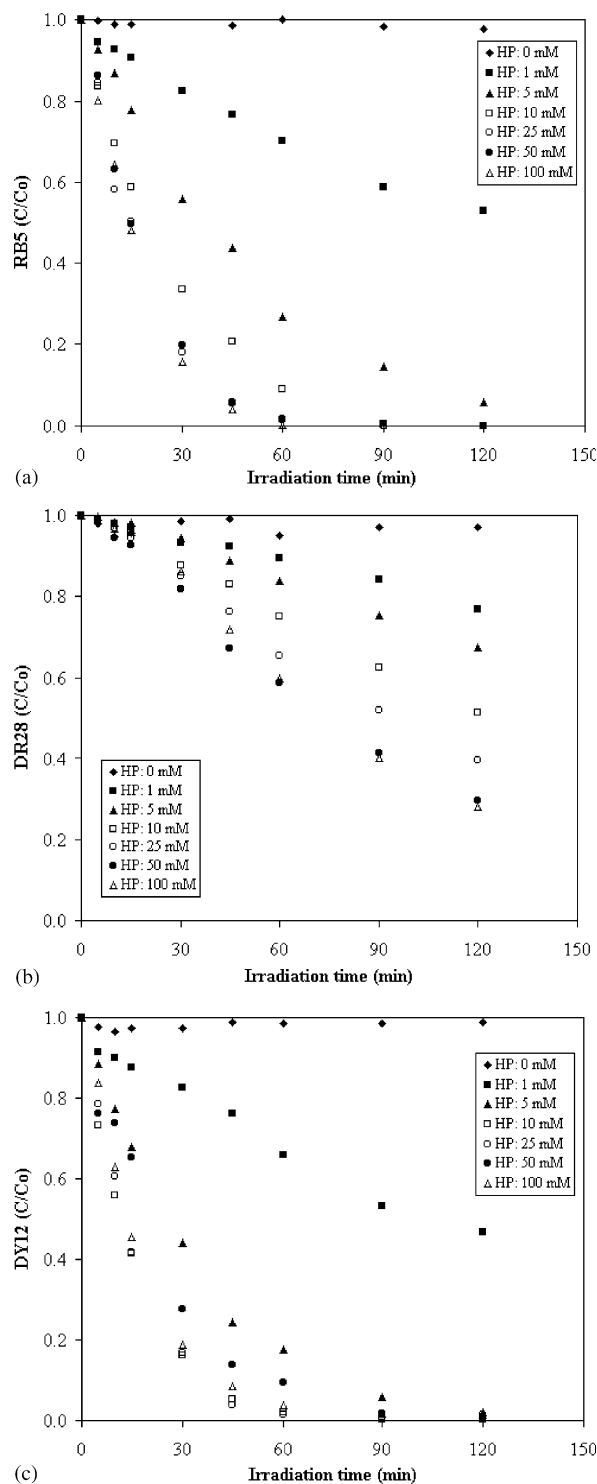


Fig. 2. Variation of residual color with irradiation time in UV/ H_2O_2 process as a function of initial hydrogen peroxide concentration (pH 7, HP: hydrogen peroxide) for: (a) C.I. RB5, (b) C.I. DR28 and (c) C.I. DY12.

same optimal concentration for RB5 was also found by some other authors [4]. C.I. DR28 showed more resistance than the others and the maximum decolorization efficiency obtained for C.I. DR28 was around 70% at a H_2O_2 concentration of 50 mM after 120 min of irradiation.

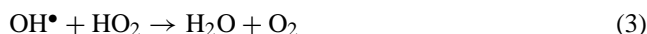
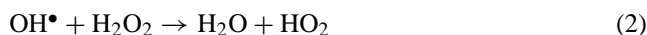
More than 50% of the color removal was observed in the first 15 min for C.I. RB5 and C.I. DY12. The decolorization efficiency for C.I. DR28 after 15 min at 50 mM H_2O_2 was only around 7%.

Variation of pH during degradation was also different for each dye. The C.I. RB5 and C.I. DY12 solutions became acidic as the pH dropped to a constant value of 3–3.5 after 45 min of irradiation. The pH value for C.I. DR28, however, was still around 5.5 after 120 min of irradiation. Decrease in pH is in accordance with those obtained by Georgiou et al. [15] and the reason of the decrease in pH can be mainly explained by two factors one of which is the oxidized intermediates that are mostly organic acids and the second factor is the production of perhydroxyl anion (HO_2^-) and H^+ produced according to the following reaction:



However, since the above reaction takes place in the alkaline pH ($\text{p}K_a$ 11.7) but the experiments have been done in natural or acidic pH, it can be concluded that the dissociation of H_2O_2 has a minor effect in pH decrease. Therefore, slight decrease in pH for C.I. DR28 can be explained with the incomplete destruction of C.I. DR28.

Another point which worth to note was the dependence of efficiency on the H_2O_2 concentration. As mentioned before, the efficiency increased with increasing H_2O_2 concentration. However, increasing the H_2O_2 concentration enhanced the oxidation process up to a certain point at which H_2O_2 started to inhibit the destruction of the dyestuff which is thought to be due to the reaction of excess H_2O_2 with OH^\bullet radicals (Reactions (2) and (3)) and thus, decreasing the amount of hydroxyl radicals which will react with the organics:



It is already well established that H_2O_2 itself acts as an effective OH^\bullet scavenger at concentrations that are specific for the pollutant in question. This is encountered during the destruction of not only dyes but also many organic compounds as well [16]. Therefore, after a certain concentration of H_2O_2 , no significant increase in decolorization efficiency was observed for all dyes. Further elevating H_2O_2 concentration, even led to decreases in color removal efficiencies (Fig. 2a–c). It can be concluded that a H_2O_2 dose higher than 25, 10 and 50 mM for C.I. RB5, C.I. DY12 and C.I. DR28, respectively corresponds to an unprofitable consumption of H_2O_2 .

The experiments with photo-Fenton process were carried out at acidic pH (pH 3). Because under acidic pH, OH^\bullet is the predominant reactive oxidant and under alkaline pH, hydroperoxyl radicals do not have as high oxidizing power as OH^\bullet [17]. Another reason for better results at lower pH is the increased iron solubility. Addition of Fe(II) to UV/ H_2O_2 process as the catalyst greatly enhanced the decolorization rate relative to UV/ H_2O_2 process. The H_2O_2 concentration was kept constant at 25 mM for all dye solutions for this

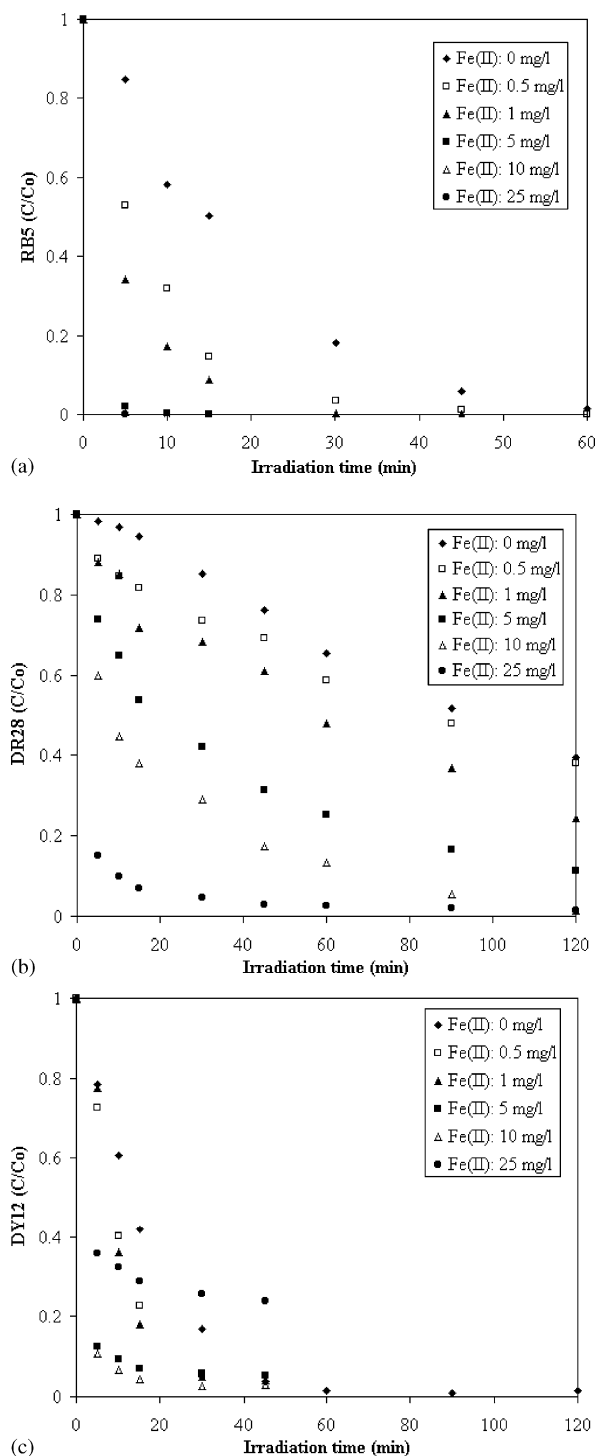


Fig. 3. Variation of residual color with irradiation time in UV/ H_2O_2 /Fe(II) process as a function of initial catalyst (Fe(II)) concentration (pH 3, H_2O_2 : 25 mM) for: (a) C.I. RB5, (b) C.I. DR28 and (c) C.I. DY12.

set of experiments. The Fe(II) concentration in photo-Fenton process was varied between 0.5 mg l^{-1} ($1 \times 10^{-2} \text{ mM}$) and 25 mg l^{-1} (0.45 mM). Fig. 3a–c illustrates the effect of initial Fe(II) concentration on the residual color for C.I. RB5, C.I. DY12 and C.I. DR28, respectively. The decolorization efficiency increased with increasing Fe(II) concentration. The

results indicate that the removal of color during the initial reaction period was quite fast in the presence of ferrous ion. The maximum efficiencies obtained and the corresponding Fe(II) concentrations after 5 min of irradiation were 98%, 5 mg l⁻¹; 88%, 5 mg l⁻¹; and 85%, 25 mg l⁻¹ for C.I. RB5, C.I. DY12 and C.I. DR28, respectively. In a study, recently carried out for the photo-Fenton oxidation of C.I. DY12 using a 8 W low-pressure mercury vapor lamp, similar removal efficiencies were achieved at longer irradiation times (20 min) and quite higher Fe(II) concentrations (Fe(II): 500 mg l⁻¹, H₂O₂: 1500 mg l⁻¹), although the concentration of C.I. DY12 was lower (50 mg l⁻¹) [18]. And this was, most probably, due to the higher power of the UV lamp used in this study (16 W). It has also been pointed out in the same study that with the increase in dye concentration, the time required for degradation also increases. At low concentration of substrate, the percentage conversion is higher compared that at higher concentration, whereas the rate of degradation increases with an increase in the initial concentration of substrate [19].

The most resistant dye in photo-Fenton process was again C.I. DR28 with only 26% removal efficiency at a Fe(II) concentration of 5 mg l⁻¹ after 5 min of irradiation when compared with the other two dyes. The increase in efficiency and the decrease in required irradiation time with increasing catalyst concentration is due to that the higher the ferrous dosage, the more the OH• can be formed through Fenton reaction, thus leading to a higher rate of color removal. It should also be noted that the removal efficiency of C.I. DY12 decreased from 88 to 64% as the concentration of Fe(II) was increased from 5 to 25 mg l⁻¹ which is thought to be due to the production of excess OH• radicals and its reaction with H₂O₂ (Reactions (2) and (3)). The question is why did not this happen in case of C.I. RB5 and C.I. DR28. The reason is, most probably, lying under the concentration of H₂O₂ applied. It is important to note that the optimal H₂O₂ concentrations in UV/H₂O₂ process were 25 and 50 mM for C.I. RB5 and C.I. DR28, respectively. However, for C.I. DY12, this concentration was 10 mM. When the concentration of H₂O₂ applied in photo-Fenton process (25 mM) was considered, it can be concluded that the decrease in removal efficiency of C.I. DY12 was due to that the H₂O₂ has been applied equal to or less than the optimal concentration for C.I. RB5 and C.I. DR28 but in excess for C.I. DY12 which led to OH• scavenging.

Most of the H₂O₂ dosage applied was consumed in the first stage of fast reaction i.e., Fenton reaction [20]. The H₂O₂ remained in the first reaction stage in turn will be decomposed through UV photolysis and determine the rest of color removal [14]. Furthermore, the highest decolorization efficiency was observed to be close to 97% for C.I. RB5 and C.I. DY12 after 30 min of irradiation for all ferrous dosages except for C.I. DY12 at 25 mg l⁻¹ Fe(II). This points out that the overall removal efficiency for all dyes makes no difference after 30 min of irradiation, in spite of the initial removal being quite different from each other for different

catalyst concentrations. The main reason for this is because the UV/H₂O₂ process of the second reaction stage further carries on the removal of color. In the first reaction stage, a lower Fe(II) dosage leads to a lower removal of color but results in a higher residue of H₂O₂. The higher the H₂O₂ concentration remained in the first reaction stage, the higher rate of color removal can be obtained in the second reaction stage. The important insight brought up here is that the dosage of H₂O₂ can govern the final removal efficiency of color in the photo-Fenton process, if the reaction is carried on for a sufficiently long time. Whereas, the ferrous dosage plays the role of catalyzing the color removal within a shorter time [14].

3.2. Mineralization studies

Since the intermediate products of some organic compounds can be more toxic and/or non-biodegradable than the original compound itself, complete destruction of such compounds should also be considered. Dyes, most of which are highly structured polymers with low biodegradability, are typical example of such compounds. Therefore, in addition to absorbance measurements for decolorization studies, TOC analysis of the same samples were also performed. Fig. 4a–c illustrates the effect of initial H₂O₂ dosage on mineralization of the three dyes in UV/H₂O₂ process. As in the case of decolorization, the removal rate of TOC increased with increasing initial H₂O₂ dosage. However, the rate of disappearance of the reactant (i.e. decolorization) was noticeably faster than that of TOC.

The maximum mineralization efficiencies obtained after 120 min of irradiation and the corresponding H₂O₂ dosages were 50%, 25 mM; 55%, 10 mM; and 12%, 50 mM for C.I. RB5, C.I. DY12 and C.I. DR28, respectively. The same trend as in the case of decolorization was observed when the initial H₂O₂ concentration was further increased. First, mineralization rates increased only slightly and at 100 mM H₂O₂, the mineralization rates started to decrease. The decrease in mineralization efficiency at 100 mM H₂O₂ when compared with the optimal values were 9 and 19% for C.I. RB5 and C.I. DY12, respectively, whereas removal efficiencies for C.I. DR28 at 50 and 100 mM H₂O₂ were almost same.

However, the maximum mineralization efficiencies obtained were not satisfactory and the reaction time required to reach these efficiencies were long. Therefore, in order to increase the mineralization efficiency and to decrease the required irradiation time, additional experiments were conducted with photo-Fenton process. Fig. 5a–c illustrates the effect of initial Fe(II) dosage on mineralization efficiency for three dyestuffs. As it can be seen, in general, increasing initial amount of iron in solution produce increasing rates of degradation. The reaction time required for almost complete mineralization of the dye solutions and the corresponding Fe(II) dosages were 45 min, 25 mg l⁻¹; 60 min, 10 mg l⁻¹; and 90 min, 25 mg l⁻¹ for C.I. RB5, C.I. DY12 and C.I. DR28, respectively.

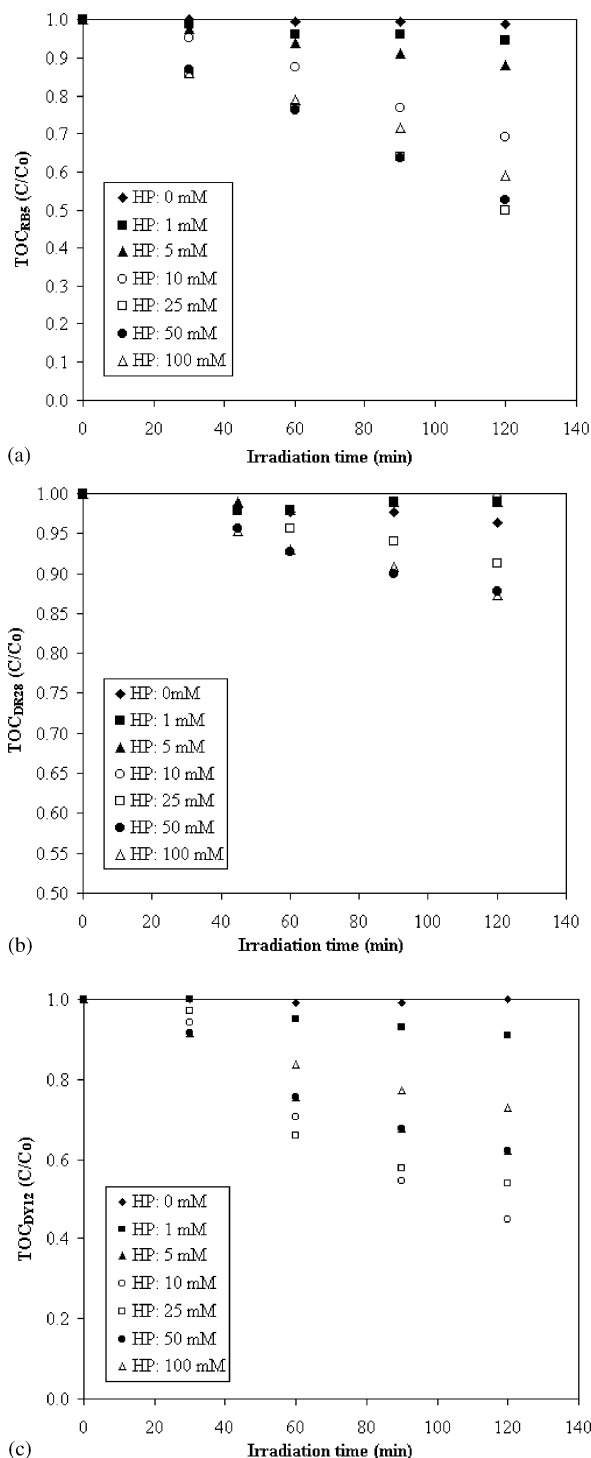


Fig. 4. Variation of residual TOC with irradiation time in UV/H₂O₂ process as a function of initial hydrogen peroxide concentration (pH 7) for: (a) C.I. RB5, (b) C.I. DR28 and (c) C.I. DY12.

3.3. Kinetic studies

Although the fast degradation of dyes in some of the experiments, especially in photo-Fenton process, required pseudo-first-order kinetics assumption, most of the degradation curves were found to obey first-order kinetics. There-

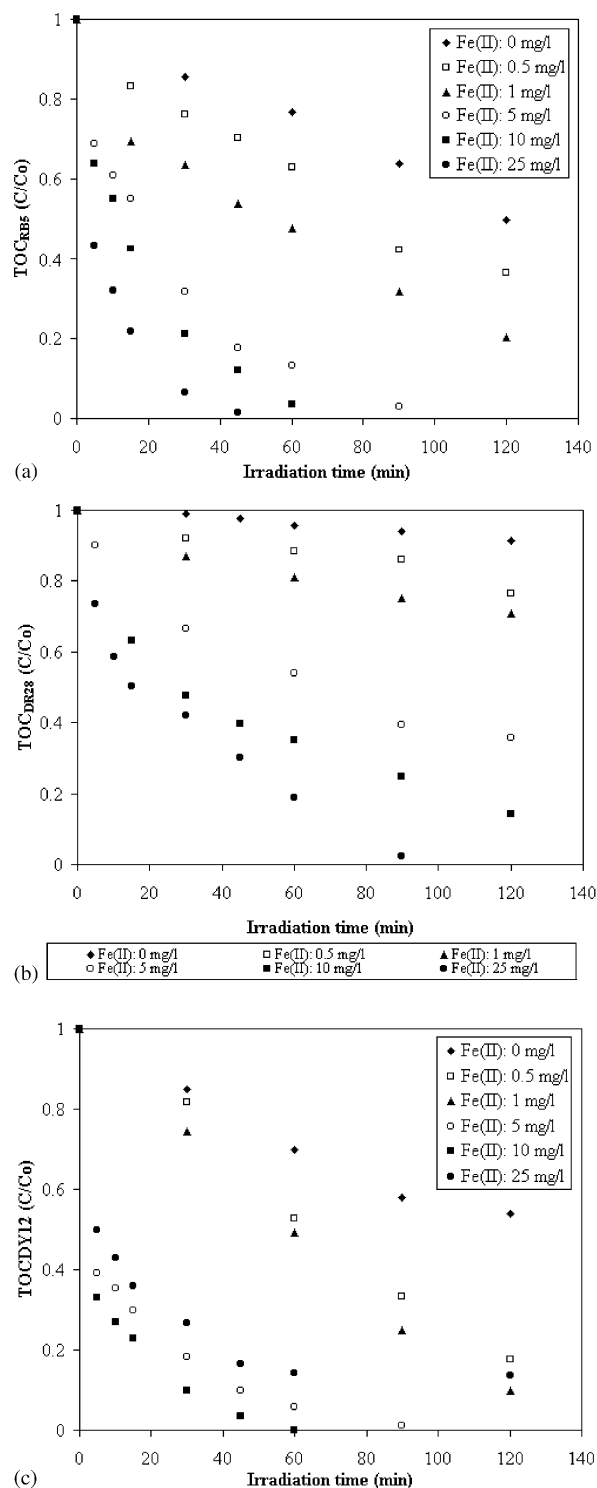


Fig. 5. Variation of residual TOC with irradiation time in UV/H₂O₂/Fe(II) process as a function of initial catalyst (Fe(II)) concentration (pH 3, H₂O₂: 25 mM) for: (a) C.I. RB5, (b) C.I. DR28 and (c) C.I. DY12.

fore, all constants were determined based on the first-order kinetics assumption (Eq. (1)). It was also assumed that the hydroxyl radical concentration was higher than the dye concentration:

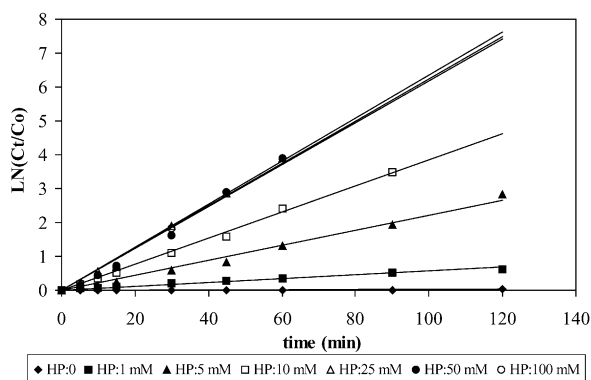


Fig. 6. A typical plot of $\ln(C_t/C_0)$ vs. time to show that the kinetic studies follows first-order reaction (process: UV/H₂O₂, pH 7, dye: C.I. RB5; C₀: 100 mg l⁻¹).

Table 2

First-order reaction rate constants and correlation coefficients of decolorization

	k (min ⁻¹) (r^2)		
	C.I. RB5	C.I. DY12	C.I. DR28
H ₂ O ₂ concentration (mM) (UV/H ₂ O ₂ process)			
1	0.0056 (0.99)	0.0063 (0.99)	0.0021 (0.99)
5	0.0222 (0.99)	0.0325 (1)	0.0033 (0.99)
10	0.0384 (0.99)	0.0771 (0.98)	0.0056 (0.99)
25	0.0634 (0.99)	0.0717 (0.99)	0.0078 (0.99)
50	0.0624 (0.99)	0.0477 (0.99)	0.0104 (0.99)
100	0.0617 (0.99)	0.0482 (0.98)	0.0109 (0.98)
Fe(II) concentration (mg l ⁻¹) (H ₂ O ₂ = 25 mM; photo-Fenton process)			
0.5	0.1131 (0.99)	0.0993 (1)	0.0063 (0.97)
1	0.1596 (0.99)	0.1036 (0.98)	0.0110 (0.99)
5	— ^a	— ^a	0.0172 (0.97)
10	— ^a	— ^a	0.0310 (0.98)
25	— ^a	— ^a	— ^a

^a Reaction rate was very fast. There was only one data between the start of the experiment and the complete disappearance of the color.

$$\ln\left(\frac{C_t}{C_0}\right) = -kt \quad (1)$$

where C₀ is the initial dye concentration, C_t the concentration of dye at time *t* and *k* the overall rate constant (time⁻¹).

Fig. 6 illustrates the typical plot of $\ln(C_t/C_0)$ versus *t* for the photodegradation of C.I. RB5 with UV/H₂O₂ process. Having the straight-line behaviour, this plot confirms the first-order reaction kinetics.

Similar plots were created for three dyes for different concentrations of H₂O₂ and Fe(II) and the determined *k* values are given in Table 2.

4. Conclusion

- The results have shown that the removal efficiency both in terms of decolorization and mineralization is negligible when UV or H₂O₂ are used alone.

- Effective decolorization by UV/H₂O₂ process is possible, however, with poor mineralization efficiency and long irradiation periods.
- The experimental results also demonstrated that the photo-Fenton process could be a suitable pre-treatment method for complete decolorization, and also mineralization of dilute effluents from textile dyeing and finishing processes, once the optimum operating conditions are established. Furthermore, photo-Fenton process greatly reduces the required irradiation times for decolorization and mineralization with respect to UV/H₂O₂ process. The H₂O₂ dosage controls the overall efficiency of both color and TOC removal, while the Fe(II) dosage plays a role of accelerating the removal, especially during the initial reaction period.
- The decolorization and mineralization efficiencies were found to increase with increasing H₂O₂ and Fe(II) concentrations, however, the marginal benefit became decreasing with further increasing of both in UV/H₂O₂ and photo-Fenton processes, respectively due to the scavenging effect of excess H₂O₂ and OH• radicals.
- Under the conditions studied, the initial rate of conversion was very high as compared to the rate later in the reaction.
- C.I. DR28 was more resistant to photodegradation with respect to C.I. RB5 and C.I. DY12.
- The kinetics of decolorization was found to follow first-order reaction rules.

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