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Degradation of azo-reactive dyes by ultraviolet radiation in the presence of hydrogen peroxide

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Abstract

This paper summarizes the results of a degradation test of several azo-reactive dyes and cotton textile wastewater under UV irradiation in the presence of H_2O_2. Five of the most commonly used azo-reactive dyes from both the Levafix and Remazol types were tested. 4-l Dye solutions of 100 mg/l were prepared immediately before irradiation. A batch mode water-jacketed immersion photoreactor was utilized. The radiation source was a 120 W UV lamp emitting at 253.7 nm and protected by a quartz tube. Complete destruction of the color of the dye solutions was succeeded in the first 20–30 min of irradiation. Almost all the aromatic rings and 80% of TOC were destroyed after 2 h of irradiation. The textile wastewater color was completely removed in less than 1 h while 90% of the aromatic rings and 70% of the wastewater COD were removed after 2 h of irradiation. UV/H_2O_2 proved capable of the complete degradation and mineralization of the above azo reactive dyes. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Azo-reactive dyes; Hydrogen peroxide; Hydroxyl radicals; Textile wastewater; Ultraviolet radiation

1. Introduction

Textile industries produce large amounts of wastewater due to high consumption of water primarily in the dyeing and finishing operations. A well-known characteristic of textile wastewater is a high content of polluting compounds. The sources of the polluting compounds when cotton is utilized are the natural impurities extracted from the fiber, the processing chemicals and dyes. The main problem occurring is that the color that remains due to the dyestuff used may cause disturbance to the ecological system of the receiving water [1–3].

Wastewater from cotton textile operations is very hard to treat by conventional activated sludge systems. The color remains due to the non-biodegradable nature of the dyes. Physical-chemical methods such as, coagulation/flocculation, activated carbon adsorption and reverse osmosis techniques have been developed in order to remove the color [4–6]. However, the latter methods can only transfer the contaminants (dyes) from one phase to the other leaving the problem essentially unsolved. Therefore, attention has to be focused on techniques that lead to the complete destruction of the dye molecules.

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Chemical oxidation using ultraviolet radiation (UV) in the presence of hydrogen peroxide (H_2O_2) is a very promising technique. UV wavelengths of 200–280 nm lead to disassociation of H_2O_2, with mercury lamps emitting at 254 nm being the most commonly used. UV/H_2O_2 systems generate hydroxyl radicals (OH) which are highly powerful oxidizing species. Hydroxyl radicals can oxidize organic compounds (RH) producing organic radicals (R), which are highly reactive and can be further oxidized. The main reactions that occur during UV/H_2O_2 oxidation are as follows [7]:

$$H_2O_2 \xrightarrow{UV} 2OHo \tag{1}$$

$$H_2O_2 \longleftrightarrow HO_2^- + H^+ \tag{2}$$

$$RH + OHo \longrightarrow H_2O + Ro \longrightarrow \text{further-oxidation} \tag{3}$$

UV/H_2O_2 systems have led to complete degradation (mineralization) and conversion to CO_2, H_2O and inorganic salts several compounds such as, aliphatic acids, alcohols, chlorinated aliphatic compounds, benzene, phenols, chlorinated phenols, pesticides and numerous others [7–12].

Several dyes utilized by textile industries (including azo-reactive ones) have also been successfully degraded by the above technique [13–15]. Azo reactive dyes are among the most commonly used to dye cotton nowadays. Therefor, the objective of this paper is to study the degradation of five different and most representative azo-reactive dyes utilized by a nearby cotton textile industry, using a UV/H_2O_2 technique. Moreover, the same technique is to be applied to wastewater obtained from the latter textile industry.

2. Experimental

2.1. Reagents

Azo-reactive dyes were obtained from DyStar (Germany). A total of five of the most representative and commonly used dyes from both the Levafix and Remazol types were tested. The characteristics of these dyes were provided by DyStar and are summarized in Table 1. The structural formulae of the reactive groups (Table 1) and also that of the Remazol Black B dye are given in Fig. 1. All dyes have a similar to the Remazol Black B dye structure, the only difference is the kind and number of reactive groups.

Textile wastewater was obtained from a nearby industry (Komotini, Greece), the characteristics of which are presented in Table 2. The sample was withdrawn from a point immediately after the equalization basin of the wastewater processing plant and it was centrifugated prior to irradiation tests in order to remove suspended particles. Analytical grade H_2O_2 (30% w/w, Fischer Scientific) was used.

2.2. Apparatus and methods

All experiments were carried out in a batch mode water-jacketed immersion photoreactor. The radiation source was an UV lamp (120 Watt, emission at 253.7 nm, manufactured by Heraeus, Germany) which was protected by a quartz tube. Temperature was maintained at 25±5 °C (temperature rose from 20 to 30 °C during the 2 h experiments). The dye solution (4 l) was projected at the bottom of the reactor and collected in a 5-l reservoir from which it was continuously pumped

Table 1
Dyes and their properties (DyStar)

Name	Azo type	Reactive group
Levafix yellow E-3GA	Monoazo	Difluorchlorpyrimidine (FCP)
Levafix red ERN	Monoazo	Monohalogentriazine (MHT)
Levafix blue EBNA	Diazo	Difluorchlorpyrimidine (FCP) Vinylsulphonyl (VS)
Remazol red RR	Monoazo	Vinylsulphonyl (VS) Monohalogentriazine (MHT)
Remazol black B	Diazo	Vinylsulphonyl×2

Table 2
Cotton textile wastewater characteristics

BOD_5 (mg/l)	COD (mg/l)	Ph	Absorbance (m^{-1})		
			436 nm	525 nm	620 nm
80	150	8.2	13.4	16.9	5.4

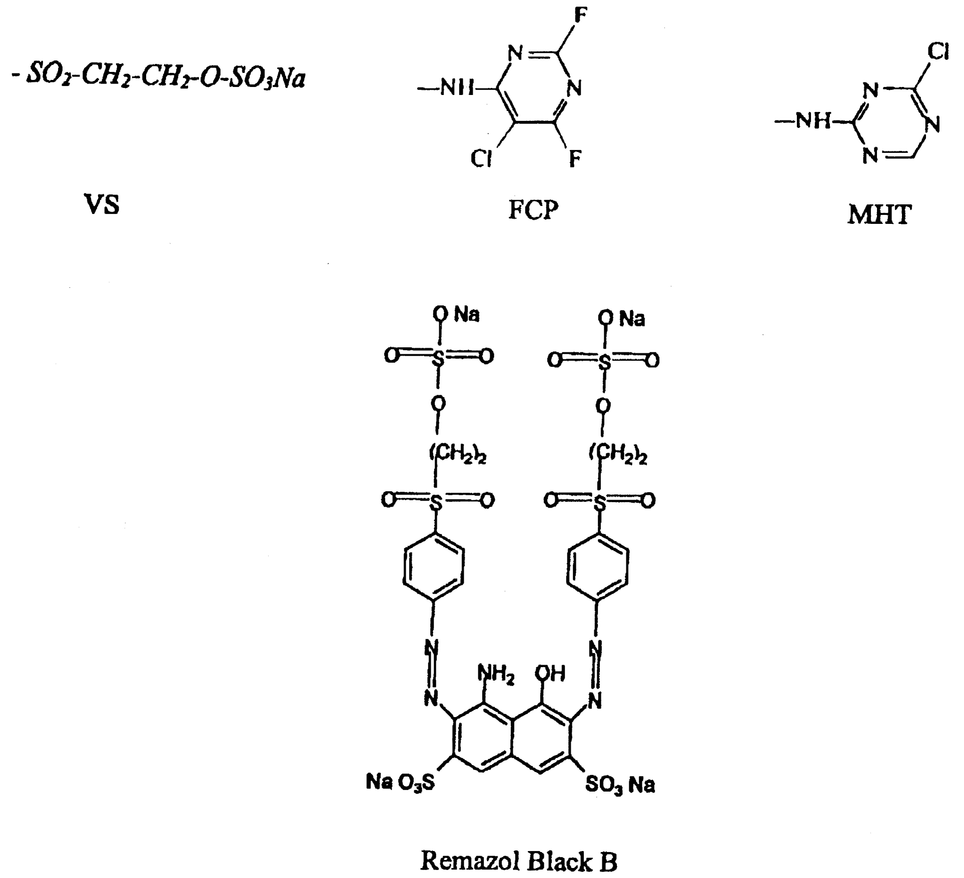

Fig. 1. The structural formulas of the reactive groups (Table 1) and the Remazol black B dye.

(250 ml/min), as shown in Fig. 2. Samples were withdrawn from the reservoir at certain time intervals and analyzed for color, absorbance at 254 nm, pH and total organic carbon (TOC) or chemical oxygen demand (COD). A UV/VIS Lambda 2S Perkin Elmer spectrophotometer and a TOC-4000 Shimadzu analyzer were utilized.

The dye solutions (100 mg/l) were prepared immediately before irradiation using deionized water.

3. Results and Discussion

The results from the irradiation tests of the Remazol black B solutions (100 mg/l) using different concentrations of H_2O_2 are summarized in Fig. 3. Even a small amount of H_2O_2 (0.1 g/l) was enough for the complete destruction of color in less than 1 h. Complete destruction of color was also achieved in less than a half-hour utilizing higher amounts of hydrogen peroxide (0.5–2 g/l). No color destruction was observed though under UV radiation in the absence of H_2O_2.

The UV–VIS spectrums of Remazol black B solution at different time intervals from a 2-h irradiation test ($H_2O_2 = 1$ g/l) are shown in Fig. 4. The visible region spectra was flattened in less than 20 min while absorbance in the UV area vanished after 120 min of irradiation.

More than 50% of color removal was observed in the first 10 min for all dye solutions. Complete removal of the color was achieved after 20–30 min of irradiation, in all cases (Figs. 5–9).

Absorbance measurements of the samples at 254 nm were taken as an indication of the aromatic

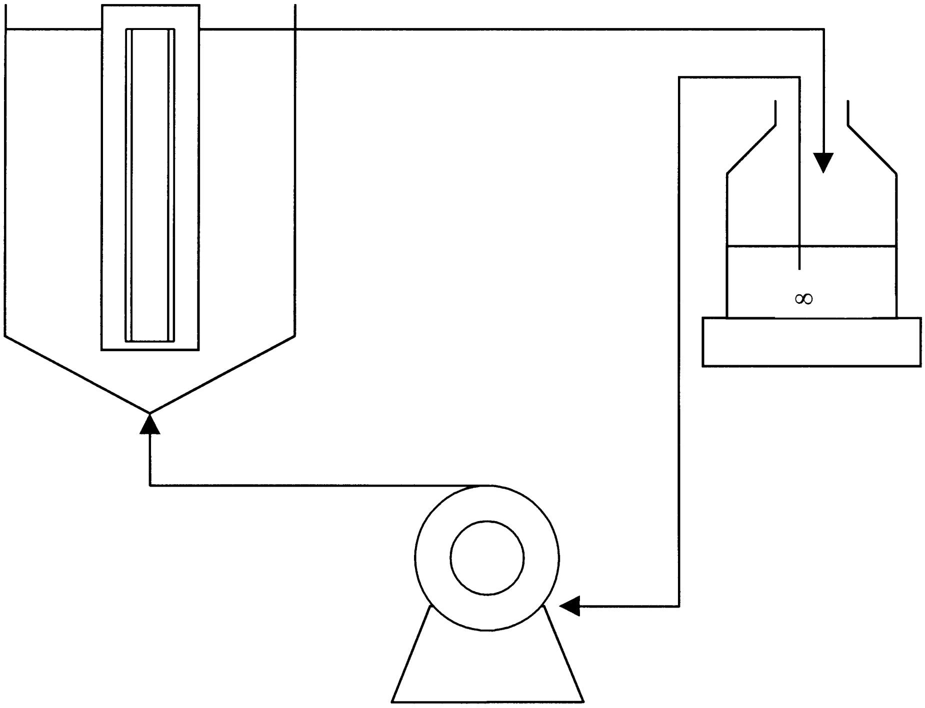

Fig. 2. Flowsheet of the UV irradiation device.

compounds' content. The destruction of the aromatic rings becomes evident in Fig. 5–9. More than 90% of the initial absorbance vanished after 2 h of irradiation.

TOC was also highly reduced in all cases. A fraction of less than 20% of the initial one remained in the end of the experiments (more than 80% removal) as shown in Fig. 5–9. It becomes evident that the reaction trend is as follows: azo reactive dyes are degraded initially resulting to intermediate products (containing aromatic rings) which in turn are further degraded to simpler products till complete degradation to CO_2, water and inorganic salts.

Fig. 10 illustrates the variation of pH with time. All dye solutions became slightly acidic as the pH dropped to a constant value of 3–3.5 after 30 min of irradiation. It is important to note that pH remained constant at its initial value ($pH_{in} = 6–7$) when one of the following, e.g. UV radiation or H_2O_2 or a dye was not present during the experiment. It is evident that under UV radiation the existence of the perhydroxyl anion (HO_2^-) becomes important [reaction (2)]. Moreover, no color destruction was observed in the absence of UV radiation after 48 h of experiment.

The results from the irradiation test of the cotton textile wastewater—using 1 g/l H_2O_2—are summarized in Fig. 11. It is interesting to note here that, even though the total dye concentration in the wastewater was at least 5 times less than the one in the previously tested dye solutions, almost the same or more time was needed for the complete destruction of the wastewater color. That was due to the non-selective nature of the hydroxyl radical (OH) reactivity (e.g. hydroxyl radicals also reacted with and were consumed by other organic compounds present in the wastewater such as the natural impurities extracted from the cotton fiber, sizes, detergents and finishing chemicals).

The rise of COD in the first 20 min of irradiation was attributed to the destruction of the dye molecules to simpler compounds that are less resistant to chemical oxidation. Finally, almost 70% of the COD and more than 90% of the aromatic content of the textile wastewater were removed after 2 h of irradiation (Fig. 11).

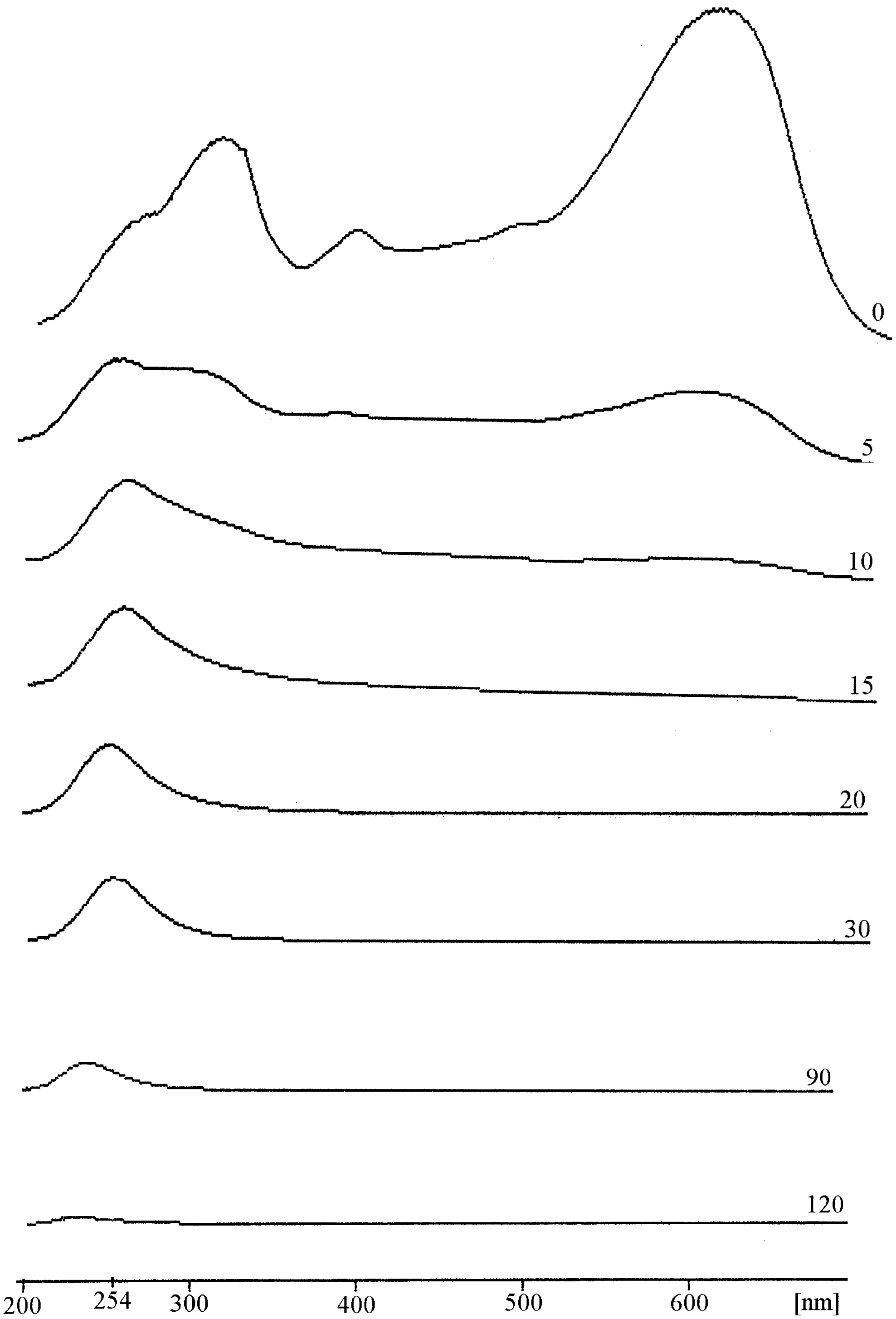

Fig. 3. UV/VIS spectrums of Remazol black B vs. time (min).

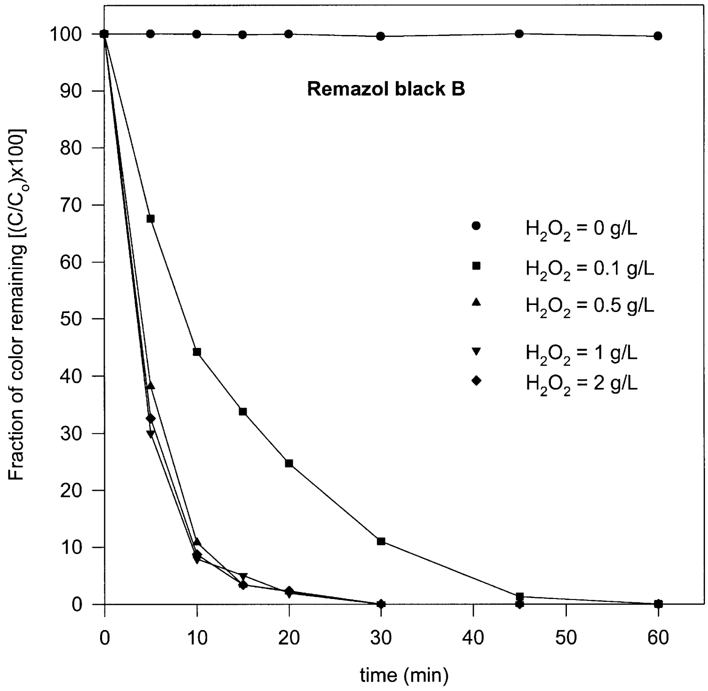

Fig. 4. UV irradiation tests of Remazol black B with various H_2O_2 concentrations.

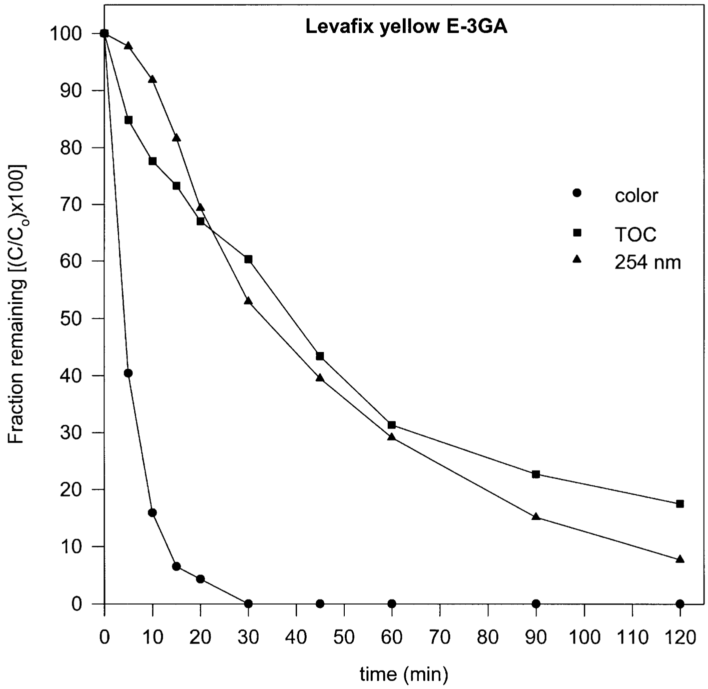

Fig. 5. UV irradiation of Levafix yellow E-3GA (H_2O_2 = 1 g/l).

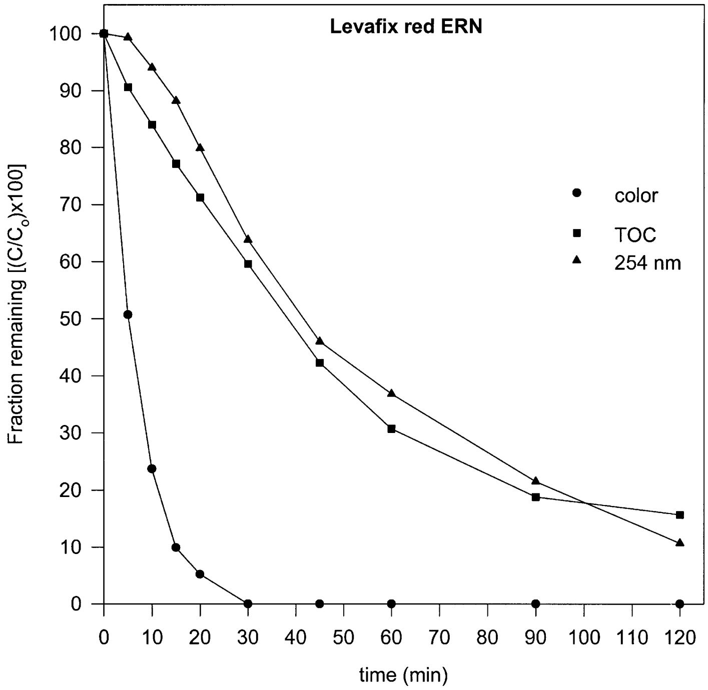

Fig. 6. UV irradiation of Levafix red ERN (H_2O_2 = 1 g/l).

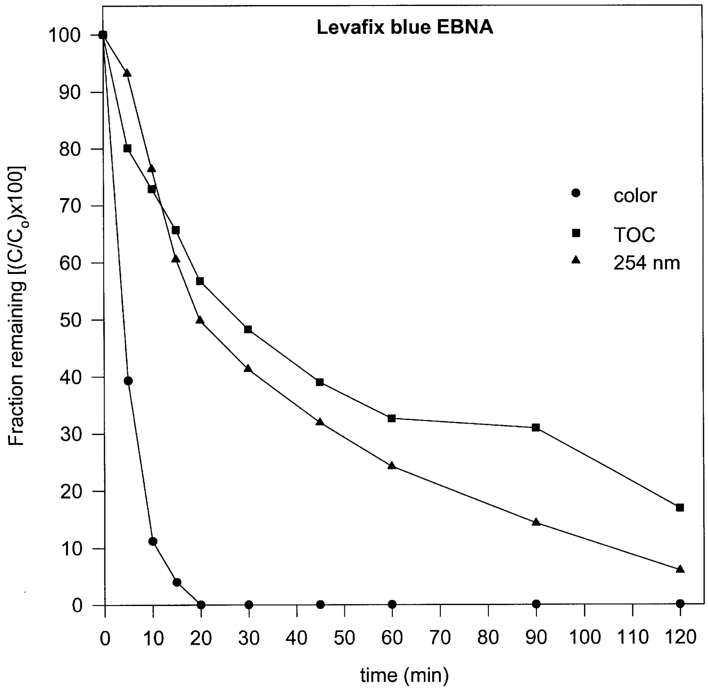

Fig. 7. UV irradiation of Levafix blue EBNA (H_2O_2 = 1 g/l).

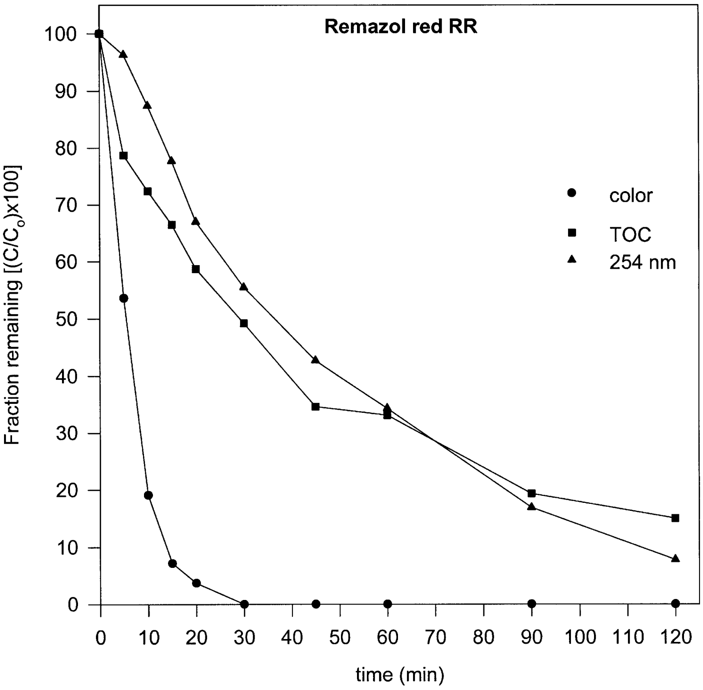

Fig. 8. UV irradiation of Remazol red RR ($H_2O_2 = 1$ g/l).

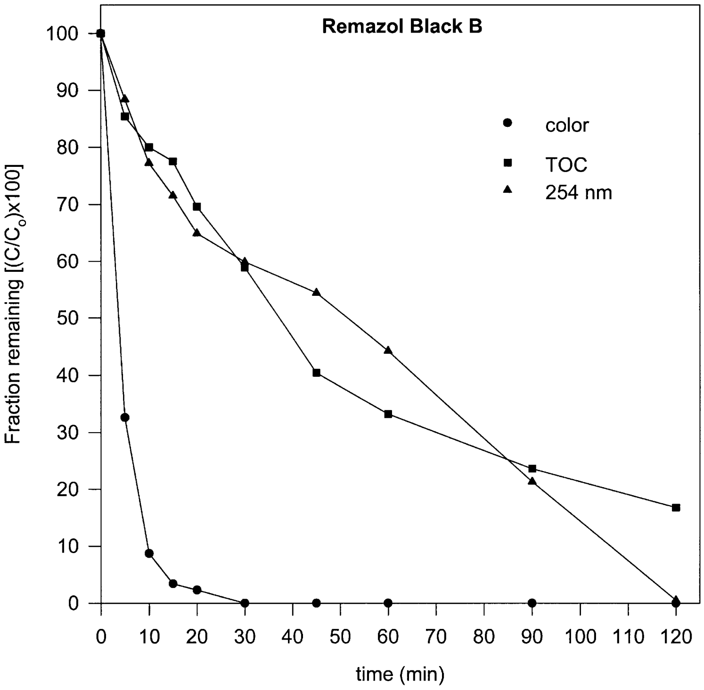

Fig. 9. UV irradiation of Remazol black B ($H_2O_2 = 1$ g/l).

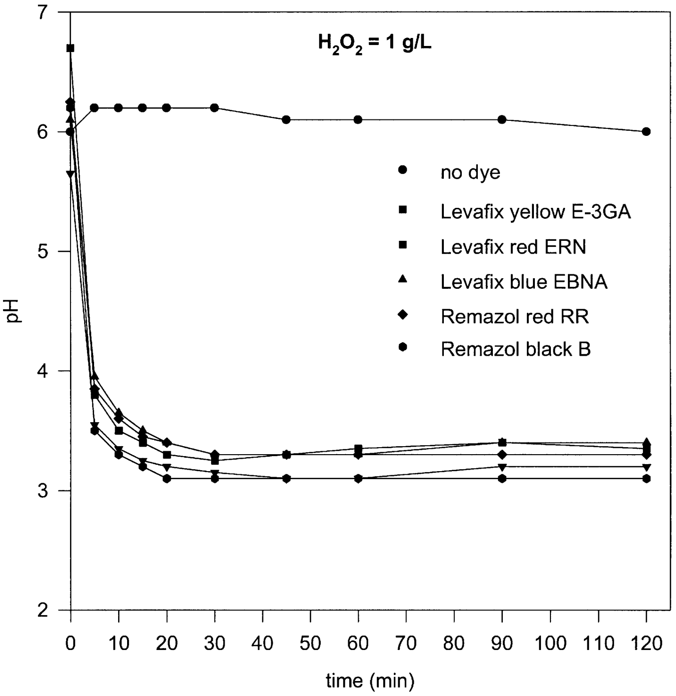

Fig. 10. The variation of pH with time.

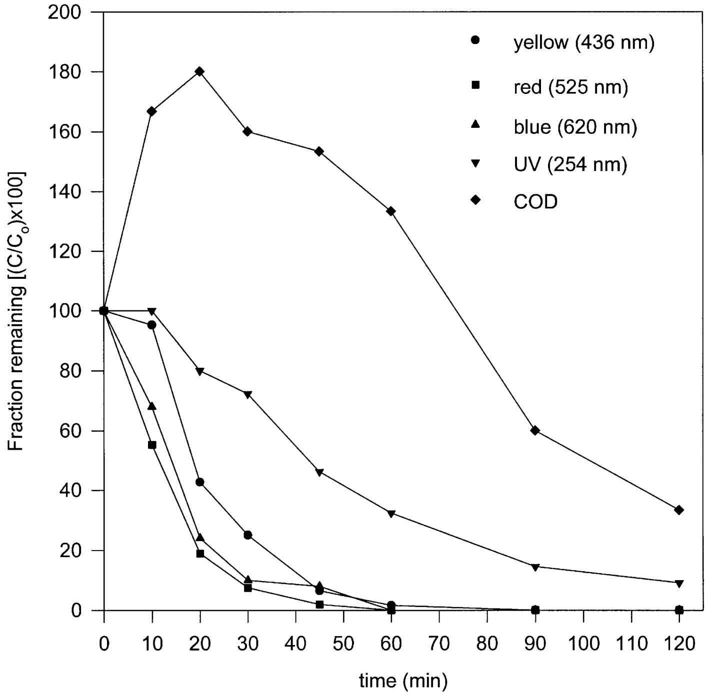

Fig. 11. UV irradiation test of the cotton textile wastewater.

4. Conclusion

The degradability of five of the most commonly used azo-reactive dyes under UV/H_2O_2 conditions was examined. Dye solutions of 100 mg/l were prepared immediately before irradiation. A batch mode water-jacketed immersion photoreactor was utilized. The radiation source was a 120 W UV lamp emitting at 253.7 nm and protected by a quartz tube. Complete destruction of the color was succeeded in the first 20–30 min of irradiation. Almost all the aromatic rings and 80% of TOC were destroyed after 2 h of irradiation. UV/H_2O_2 is capable of the complete mineralization of the above azo reactive dyes. The same technique was also applied to cotton textile wastewater. Complete color removal was achieved in less than 1 h while 90% of the aromatic rings and 70% of the wastewater COD were removed after 2 h of irradiation.

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