



Evaluation of UV/H₂O₂ advanced oxidation process (AOP) for the degradation of diazo dye Reactive Green 19 in aqueous solution

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Received 17 January 2013; Accepted 14 March 2013

ABSTRACT

The azo dye Reactive Green 19 (RG19) is extensively used for dyeing textiles due to its cost effectiveness and excellent fastness properties. Treatment of wastewaters containing this dye by conventional methods is often inadequate because of its resistance to biological and chemical degradation. In this study, the suitability of an advanced oxidation process based on the use of UV radiation and hydrogen peroxide to degrade RG19 was investigated. Analysis of degradation data showed that the decolorization process followed pseudo-first-order kinetics. The existence of an optimum pH and H₂O₂ dose was also observed. Under the best conditions, complete decolorization of the dye solution was achieved in about 20 min. Total organic carbon (TOC) measurements showed that mineralization was slower than decolorization, but over 63% of TOC was removed in 90 min. Overall, the results obtained indicate that the UV/H₂O₂ treatment can be an effective method for the removal of RG19 from textile effluents.

Keywords: Reactive Green 19; Azo dye; Photodegradation; UV/H₂O₂; Advanced oxidation processes (AOP); Wastewater

1. Introduction

Reactive Green 19 (RG19) is a sulfonated diazo dye with a high molecular weight ($M_w = 1418.9 \text{ g mol}^{-1}$) and a chemical structure characterized by the presence of two azo groups as the chromophoric moiety and two chlorotriazine groups (Fig.1). The use of RG19 for textile dyeing has increased steadily over the last few years because of its cost effectiveness and excellent wash and light fastness properties. However, like other azo dyes, RG19 exhibits a very low degree of fixation on the fiber, typically between 50 and 90% [1], which

results in the release of substantial amounts of the compound in the dyeing water.

The high aromaticity and low reactivity of RG19 make this dye highly resistant to both microbial and chemical degradation. For example, more than 40 h were necessary to completely degrade the dye at 37°C and initial concentration of 50 mg L⁻¹ using the microbial species *Micrococcus glutamicus* [2]. In another study carried out with an aerobic bacterial consortium isolated from dye-contaminated soils, a maximum color reduction of about 80% was observed [3]. On the other hand, a comparative study on seven azo dyes

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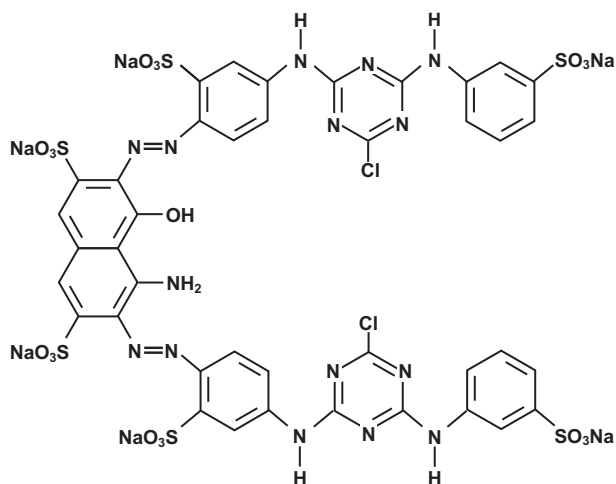


Fig. 1. Chemical structure of RG19.

treated by *Aeromonas hydrophila* showed that RG19 was the least susceptible to degradation, with a reported efficiency of only 7–14% [4]. Low degradation efficiencies were also observed by using the UV/TiO₂ oxidation process, which gave a maximum removal of 70% for a 4h treatment at an initial dye concentration of 10 g L⁻¹ [5]. These results clearly demonstrate that RG19 is recalcitrant to degradation and that there is a need to explore more effective methods for removing it from textile effluents.

This study was undertaken to evaluate the applicability of the UV/H₂O₂ process to degrade RG19 in water. This method belongs to the so-called advanced oxidation processes (AOPs), which are considered among the most effective technologies for the degradation of refractory organic pollutants [6–9]. AOPs are based on in situ generation of highly reactive radical species that are capable of degrading the contaminants by the use of solar, chemical, or other forms of energy [10]. In the case of the UV/H₂O₂ process, the hydroxyl radicals (HO[•]) generated from the photolysis of hydrogen peroxide are the main reactive species responsible for oxidation [11]. They attack the target organic molecules causing their destruction and final mineralization to carbon dioxide, water, and harmless inorganic ions.

The application of the UV/H₂O₂ method to the treatment of wastewaters containing organic pollutants has been extensively investigated in the last years because of some inherent advantages over other AOPs, such as easy handling, high stability, commercial availability of hydrogen peroxide, and no sludge formation [12–14]. Studies on azo dyes have shown that the degradation efficiency depends on several factors, including the irradiance level, the pH, the

hydrogen peroxide to dye molar ratio, and the chemical structure of the dye [15–17]. In particular, polyazo dyes are less sensitive to oxidation than monoazo ones, but the nature of auxiliary groups attached to the aromatic nuclei in the dye molecule also plays a key role [18]. In addition, although the UV/H₂O₂ process is capable of destroying quite quickly the chromophore structure of azo dyes, i.e. to decolorize the dye solution, the rate of dye mineralization is much lower than that of decolorization. Evidence also indicates that in most cases an optimal H₂O₂ dosage exists that allows for improving the process performance and reducing the operating costs. As a result, the applicability of this approach for a given dye system should be considered on a case-by-case basis.

In order to assess the ability of the UV/H₂O₂ process to remove RG19 from textile effluents, the kinetics of dye degradation in aqueous solution was studied and the effects of dye concentration, hydrogen peroxide dose, and pH value on the degradation efficiency were determined. The extent of RG19 mineralization under the tested conditions was also investigated.

2. Experimental materials and methods

2.1. Materials

RG19 was obtained as a solid powder from Gammacolor Srl (Seveso, Italy) and used without further purification. Hydrogen peroxide (30% v/v aqueous solution) was purchased from Sigma Chemical (Milano, Italy). Working peroxide solutions were prepared by diluting the stock solution with double-distilled water. Their concentrations were checked spectrophotometrically at 240 nm using a molar extinction coefficient of 43.6 M⁻¹ cm⁻¹ [19]. The pH of the solution was adjusted to the desired value by addition of H₂SO₄ or NaOH.

2.2. Photodegradation experiments

Experiments to investigate the photodegradation kinetics of RG19 were carried out in a cabinet maintained at 20 ± 2°C and equipped with a low-pressure mercury lamp (Spectroline ENF-260C/FE, Spectronics Corp., USA). The UV source had a nominal power of 6 W and a maximum emission at 254 nm. Rectangular quartz cells (Hellma, Germany) with an internal volume of 4 mL and an optical path length of 1 cm were inserted in the cabinet at calibrated distances from the lamp, with the exposed surface perpendicular to the direction of light propagation. To ensure a stable light emission, the lamp was warmed up for at least 10 min before starting the experiment. The irradiance

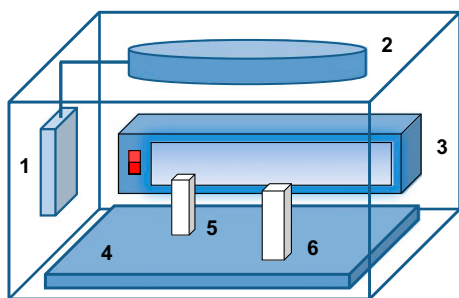


Fig. 2. Schematic of the apparatus used for photodegradation experiments (1—Temperature controller; 2—Forced-air ventilation system; 3—UV lamp; 4—Magnetic stirrer plate; 5, 6—Quartz cells at selected distances from the UV source).

level at the selected distance was periodically checked by using a radiometer equipped with a UV-C sensor (AccuMax XR-1000, Spectronics Corp. US). A schematic of the experimental setup is shown in Fig. 2.

In a typical run, the RG19 solution with or without hydrogen peroxide was poured in the quartz cell and irradiated for the prescribed time. At the end of exposure, the cell was taken out and the absorption spectrum of the dye was recorded. Measurements were performed with a double-beam spectrophotometer (Lambda 25, Perkin Elmer, US) against a blank consisting of the same test solution but without RG19.

The initial dye concentration in the solution was 90 mg L^{-1} ($6.34 \times 10^{-5} \text{ M}$), the intensity of UV radiation was set at $1,500 \mu\text{W cm}^{-2}$, the H_2O_2 concentration was varied between 2.5 and 120 mM, and the pH between 2 and 10.

Preliminary experiments showed that the increase in the temperature of the irradiated solution over the time period of interest was always $<1^\circ\text{C}$. It was also verified that no loss of RG19 via hydrolysis or other degradation processes occurred in the absence of H_2O_2 and UV irradiation.

Total organic carbon (TOC) measurements were made with a Shimadzu analyzer (TOC-5000A, Shimadzu Corp., Japan) equipped with an IR detector and an autosampler.

3. Results and discussion

Fig. 3 shows the absorption spectrum of RG19 in the range 200–900 nm and the spectral changes occurring during the UV/ H_2O_2 treatment. It can be seen that the dye spectrum is characterized by two main bands, one in the UV region ($\lambda_{\text{max}}=272 \text{ nm}$) and the other in the visible region ($\lambda_{\text{max}}=630 \text{ nm}$). The 272 nm band arises from the aromatic rings in the dye molecule, while the 630 nm band is due to the azo bonds

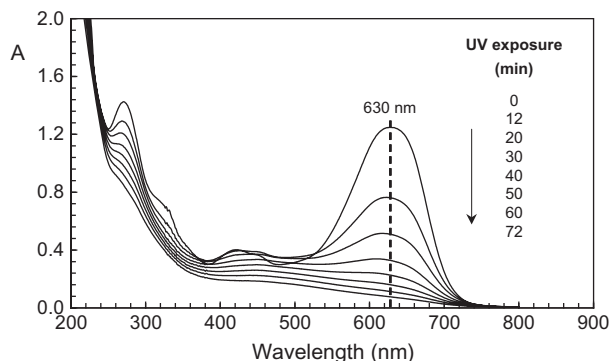


Fig. 3. Absorption spectra of RG19 at various irradiation times ($c_{d0}=6.34 \times 10^{-5} \text{ M}$; $c_h=1.25 \text{ mM}$; $I_0=1,500 \mu\text{W cm}^{-2}$; $\text{pH}=6.5$).

($-\text{N}=\text{N}-$), which are responsible for the green color. When RG19 was treated by UV/ H_2O_2 , the intensities of both bands decreased suggesting that decolorization was accompanied by at least partial degradation of the aromatic ring structures. To study the kinetics of dye removal, the absorbance change at 630 nm was monitored. Absorbance values were converted into RG19 concentrations by using an extinction coefficient of $20.6 \text{ mM}^{-1} \text{ cm}^{-1}$ ($1.45 \times 10^{-2} \text{ mg}^{-1} \text{ L cm}^{-1}$), which was determined from a calibration curve derived from standard dye solutions.

The experimental data presented in Fig. 4 indicate that neither H_2O_2 nor UV alone had appreciable effects on the removal of RG19. In contrast, significant dye degradation was observed when they were applied simultaneously.

Photodegradation experiments were carried out by irradiating a dye solution contained in a 4 mL quartz cell. The use of such a small reaction volume allows

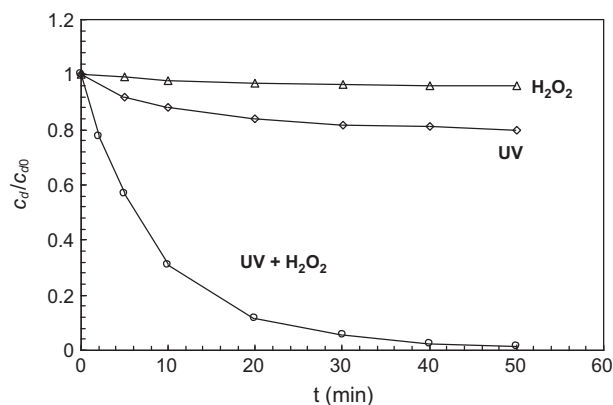


Fig. 4. Effect of UV, H_2O_2 , and UV/ H_2O_2 on the concentration of RG19, calculated from the absorbance changes at 630 nm ($c_{d0}=6.34 \times 10^{-5} \text{ M}$; $c_h=2.5 \text{ mM}$; $I_0=1,500 \mu\text{W cm}^{-2}$; $\text{pH}=6.5$).

for minimizing temperature and concentration inhomogeneities within the system. Accordingly, the estimated kinetic parameters can be considered representative of the true or intrinsic photodegradation kinetics [20,21]. A simplified reaction scheme for the H_2O_2 -assisted photodegradation is the following:



which assumes that the dye molecule is attacked by both UV photons and the HO^\bullet generated from the photolysis of H_2O_2 to give the final products. The rate of dye removal can therefore be expressed as the sum of the contributions of the direct and H_2O_2 -assisted photodegradation:

$$r = k_{\text{UV}}c_{\text{d}}^a I_0^b + k_{\text{UV}/\text{H}_2\text{O}_2}c_{\text{d}}^c c_{\text{h}}^d I_0^e \quad (4)$$

where c_{d} and c_{h} are the concentrations of dye and H_2O_2 , respectively, I_0 is the intensity of UV radiation, k_{UV} and $k_{\text{UV}/\text{H}_2\text{O}_2}$ are the rate constants for the two processes and $a-e$ are apparent reaction orders.

Considering that: (a) the contribution of direct UV photolysis to RG19 degradation was much smaller than that of the H_2O_2 -assisted process, as can be seen from an examination of Fig. 4 and a comparison of the corresponding rate constants; (b) the intensity of UV radiation was kept constant; and (c) the concentration of H_2O_2 undergoes only minor changes during the $\text{UV}/\text{H}_2\text{O}_2$ treatment [15,22,23], Eq. (1) simplifies to:

$$r = kc_{\text{d}}^c \quad (5)$$

where k , the apparent rate constant, is given by:

$$k = k_{\text{H}_2\text{O}_2/\text{UV}}c_{\text{h}}^d I_0^e \quad (6)$$

As a result, the mass balance for the degrading dye in the aqueous solution can be written as:

$$-\frac{dc_{\text{d}}}{dt} = kc_{\text{d}}^c \quad (7)$$

Integration of Eq. (7) with the initial condition: $c_{\text{d}}(0) = c_{\text{d}0}$ provides the dye concentration decay in the liquid as a function of time. Concentration data plotted against time on a semi-log scale yielded straight lines (Fig. 5), indicating that the degradation

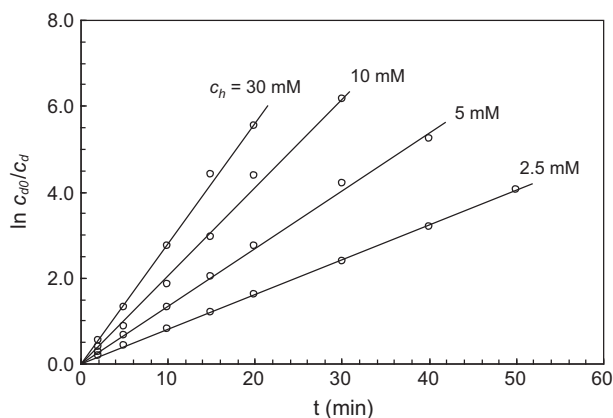


Fig. 5. Semi-log plots for dye concentration decay ($c_{\text{d}0} = 6.34 \times 10^{-5} \text{ M}$; $I_0 = 1,500 \mu\text{W cm}^{-2}$; $\text{pH} = 6.5$).

process followed pseudo-first-order kinetics. Under these conditions, the integration of Eq. (7) gives:

$$\ln\left(\frac{c_{\text{d}}}{c_{\text{d}0}}\right) = -kt \quad (8)$$

Accordingly, the first-order rate constants were determined from the slope of the corresponding straight lines. Then, the times required to achieve 95% (t_{95}) and 99% (t_{99}) dye removal were calculated by setting $c_{\text{d}}/c_{\text{d}0} = 0.05$ and 0.01, respectively, in the above equation, so as to obtain:

$$t_{95} = -\frac{\ln 0.05}{k} \quad (9)$$

$$t_{99} = -\frac{\ln 0.01}{k} \quad (10)$$

From the results presented in Table 1, it can be seen that the application of $\text{UV}/\text{H}_2\text{O}_2$ caused a rapid decolorization of the dye solution, 15–60 min being sufficient to achieve 99% RG19 removal. Moreover, the rate of dye disappearance increased with the initial H_2O_2 concentration until reaching a maximum at $c_{\text{h}} = 30 \text{ mM}$. Further increases in H_2O_2 concentration resulted in an almost linear decrease of the degradation rate (Fig. 6).

The existence of an optimum H_2O_2 concentration has been reported in several other studies on azo dyes [13, 24–26]. It can be explained as follows. If more hydrogen peroxide is present in the irradiated solution, more HO^\bullet radicals are available for dye degradation (Eq. (2)), with a positive effect on the decolorization rate. At high concentrations, however, hydrogen peroxide can scavenge HO^\bullet according to the reaction [27]:

Table 1

First-order rate constants (k) and time required to achieve 95% (t_{95}) and 99% (t_{99}) dye removal for different H_2O_2 concentrations (c_h). Other conditions: $c_{d0} = 6.34 \times 10^{-5} \text{ M}$; $I_0 = 1,500 \mu\text{W cm}^{-2}$; $\text{pH} = 6.5$

c_h (mM)	k (min^{-1})	t_{95} (min)	t_{99} (min)
2.5	0.079 ± 0.003	38.0 ± 1.6	58.4 ± 2.5
5	0.138 ± 0.006	21.7 ± 0.9	33.4 ± 1.4
10	0.210 ± 0.007	14.2 ± 0.5	21.9 ± 0.7
20	0.261 ± 0.005	11.5 ± 0.2	17.7 ± 0.3
30	0.285 ± 0.007	10.5 ± 0.2	16.1 ± 0.4
40	0.274 ± 0.002	10.9 ± 0.1	16.8 ± 0.1
60	0.246 ± 0.013	12.2 ± 0.6	18.7 ± 1.0
80	0.218 ± 0.005	13.6 ± 0.3	20.8 ± 0.5
120	0.164 ± 0.007	18.2 ± 0.8	28.0 ± 1.2



Since HO_2 radicals are much less reactive than $\text{HO} \cdot$, the rate of dye destruction would progressively decrease. Furthermore, higher H_2O_2 concentrations would absorb more UV light ($\epsilon_{\text{H}_2\text{O}_2} = 19.6 \text{ M}^{-1} \text{ cm}^{-1}$ at 254 nm), exerting a screening effect that reduces the degradation of the dye. A combination of these effects could be responsible for the observed maximum in the k vs. c_h curve (Fig. 6).

To determine the effect of pH on dye degradation, experiments at the optimum H_2O_2 concentration (30 mM) were carried out by varying the initial pH of the solution between 2 and 10. The results reported in Fig. 7 indicate that there exists an optimum pH value, around 6, for the removal of RG19. At this pH, the times required to degrade 95 and 99% of the dye were about 11 and 17 min, respectively.

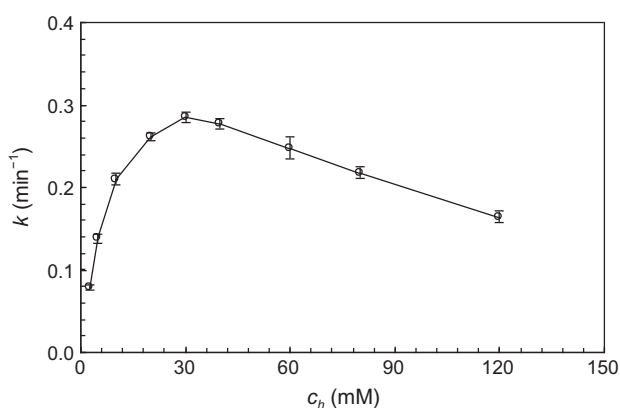


Fig. 6. Effect of H_2O_2 concentration (c_h) on the first-order rate constants (k) ($c_{d0} = 6.34 \times 10^{-5} \text{ M}$; $I_0 = 1,500 \mu\text{W cm}^{-2}$; $\text{pH} = 6.5$).

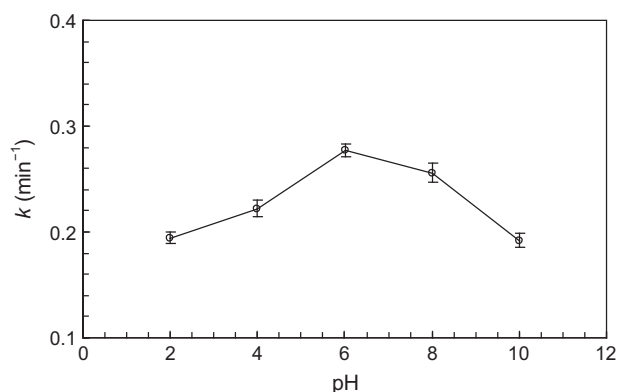
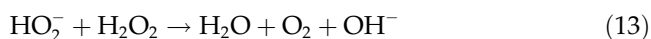


Fig. 7. Effect of initial pH on the first-order rate constants (k) ($c_{d0} = 6.34 \times 10^{-5} \text{ M}$; $c_h = 2.5 \text{ mM}$; $I_0 = 1,500 \mu\text{W cm}^{-2}$).

The presence of a maximum in the pH dependence of the degradation rate is most likely the result of different competing effects [17,28,29]. One of them originates from the deprotonation of hydrogen peroxide to form HO_2^- :

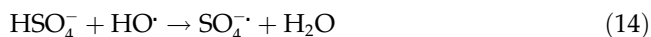


which proceeds more rapidly under alkaline conditions. When irradiated by UV light, the HO_2^- species give rise to the formation of dioxygen and water, rather than $\text{HO} \cdot$:



As a result, the concentration of $\text{HO} \cdot$ in the aqueous solution decreases, together with the rate of dye degradation.

At the other extreme, i.e. acidic conditions, the presence of large amounts of HSO_4^- ions can negatively affect the degradation rate of RG19 because of the formation of inorganic radical anions ($\text{SO}_4^{\cdot-}$) from $\text{HO} \cdot$:



These inorganic radical ions are much less reactive than $\text{HO} \cdot$, causing a drop in the decolorization efficiency.

Finally, strong electrolytes such as NaOH and H_2SO_4 can promote the aggregation of dye molecules, especially those containing sulfonic groups [30]. Since these aggregates are less accessible to $\text{HO} \cdot$ than single molecules, their degradation would be more problematic.

To evaluate the degree of dye mineralization, the TOC values of the irradiated dye solution under optimum H_2O_2 and pH conditions ($c_h = 30 \text{ mM}$, $\text{pH} = 6.5$)

were measured. The percent variations in TOC (ΔTOC) at 15, 30, 60, and 90 min were: $\Delta\text{TOC}_{15} = 13.5\%$, $\Delta\text{TOC}_{30} = 25.8\%$, $\Delta\text{TOC}_{60} = 48.2\%$, and $\Delta\text{TOC}_{90} = 63.5\%$. These results indicate that the rate of dye mineralization is lower than that of decolorization. In fact, while the dye solution was almost completely decolorized in about 20 min, higher time periods were necessary to mineralize the dye under the same process conditions. This may be due to the higher stability of the aromatic ring structures in the dye molecule, compared to the azo bond regions, and/or to their ability to stabilize intermediates formed during photolysis [28,31,32]. However, the above results suggest that mineralization can be significantly improved by prolonging the duration of the treatment.

It may be interesting to compare the present results with those obtained in the few other studies on RG19 degradation. Farajzadeh et al. [5] investigated the photocatalytic degradation of RG19 in a rectangular photoreactor containing TiO_2 nanoparticles immobilized on ceramic plates and a UV-C source. Under optimized conditions, an irradiation time of 4 h was required to achieve a decolorization efficiency of 70%. Dye mineralization was monitored by chemical oxygen demand (COD) decrease and by changes in the UV-vis spectrum. Under the conditions found to be optimum for decolorization, COD was reduced by over 90% after a 9 h treatment. In the study of Senan and Abraham [3], RG19 was degraded using a strain of *Pseudomonas putida* and a selected bacterial consortium consisting of two gram-negative cocci isolated from dye-contaminated soils. After 10 days from inoculation, the measured decolorization efficiency reached a value close to 80%. Lower removal degrees were observed when RG19 was in mixture with other azo dyes. The microbial degradation of RG19 by the species *M. glutamicus* was also investigated [2]. The experiments performed at 37°C and pH 8 under static anoxic conditions showed that the dye was completely decolorized within 42 h. After this time, the measured reductions in COD and TOC were 66 and 72%, respectively.

From the above, it can be concluded that the UV/ H_2O_2 treatment of RG19 can lead to removal efficiencies that are comparable or higher than those reported for photocatalytic or microbial degradation of RG19. However, compared to these two types of processes, the examined method seems to be simpler to implement and more flexible in operation. Finally, a comparison with the results obtained by applying the UV/ H_2O_2 process to other dyes [23,28] provides further support to the view that the treatment efficiency, both in terms of decolorization and mineralization, depends strongly on the nature of the dye.

Nevertheless, by appropriate selection of the process conditions, also structurally complex and recalcitrant azo dyes like RG19 can be effectively degraded by this treatment.

4. Conclusion

The results of this study indicate that AOPs based on UV/ H_2O_2 can effectively remove RG19 from textile wastewaters. Kinetic analysis of photodegradation data showed that the decolorization process followed pseudo-first-order kinetics and that optimal values exist for both pH and applied H_2O_2 dose. While complete decolorization can be obtained in about 20 min, prolonged irradiation is necessary to achieve a significant TOC removal.

In order to assess the feasibility of the process on a larger scale, further research is required focusing on the mechanisms of dye degradation and mineralization together with a detailed cost-benefit analysis.

Acknowledgments

We are grateful to Gammacolor Srl (Seveso, Italy) for the kind donation of RG19 azo dye. We also thank Dr. Elisabetta Petrucci for her technical assistance in performing TOC measurements.

Symbols

$a, b, c,$	—	apparent reaction orders
d, e	—	
c_d	—	dye concentration, mol L^{-1}
c_h	—	H_2O_2 concentration, mol L^{-1}
I_0	—	intensity of UV radiation, $\mu\text{W cm}^{-2}$
K	—	apparent rate constant, min^{-1}
k_{UV}	—	rate constant for direct photodegradation, $\text{cm}^2 \mu\text{W}^{-1} \text{min}^{-1}$
$k_{UV/\text{H}_2\text{O}_2}$	—	rate constant for H_2O_2 -assisted photodegradation, $\text{L cm}^2 \text{mol}^{-1} \mu\text{W}^{-1} \text{min}^{-1}$
r	—	degradation rate, $\text{mol L}^{-1} \text{min}^{-1}$
t	—	time, min
t_{95}	—	time for 95% dye removal, min
t_{99}	—	time for 99% dye removal, min
$\varepsilon_{\text{H}_2\text{O}_2}$	—	H_2O_2 extinction coefficient, $\text{L mol}^{-1} \text{cm}^{-1}$

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