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Role of HO· and SO$_4^-$· radicals on the photodegradation of remazol red in aqueous solution

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HIGHLIGHTS

- Results obtained demonstrate UV radiation to be unable to degrade RR.
- Sulfate radicals have a greater selectivity to degrade the RR molecule in comparison to HO· radicals.
- A greater reduction in TOC$_{60}$ by SO$_4^-$· radicals in ultrapure water and by HO· radicals in natural waters.
- The toxicity of degradation by-products largely depends on the process used.

ARTICLE INFO

ABSTRACT

The aim of this study was to determine the effectiveness of oxidation processes (AOPs) based on the use of UV radiation (UV, UV/H$_2$O$_2$, and UV/K$_2$S$_2$O$_8$) in the degradation and mineralization of dye remazol red (RR) in aqueous solution. Results showed that ultraviolet (UV) radiation was unable to degrade RR and that addition of H$_2$O$_2$ or K$_2$S$_2$O$_8$ during the photodegradation markedly accelerated oxidation of this dye. The effectiveness of the UV/H$_2$O$_2$ system to remove RR was favored at low H$_2$O$_2$ concentrations, low dye concentrations, and high temperatures. Thus, the results obtained show that the decolorization process becomes slower with higher dye concentrations; thus, 99.9%, 81.0%, and 47.7% decolorization was obtained after 60 min when using initial concentrations of 20, 50, and 100 mg/L. Results obtained show that the degradation kinetics at 288 and 298 K were very similar, achieving 66% decolorization at both temperatures after 60 min of treatment. Decolorization kinetics were not accelerated at high H$_2$O$_2$ concentrations, but there was an increase in organic matter mineralization. Apparent reaction rate constants were around 2.5-fold higher with the UV/K$_2$S$_2$O$_8$ system than with the UV/H$_2$O$_2$ system. The results obtained indicate that RR molecules are more selectively degraded by SO$_4^-$· radicals than by HO· radicals. The k_{AP} values and TOC reduction were higher with the UV/S$_2$O$_8^{2-}$ system than with the UV/H$_2$O$_2$ system in ultrapure water but the inverse was observed in natural waters, when higher values were obtained with the UV/H$_2$O$_2$ than with the UV/S$_2$O$_8^{2-}$ system. Results obtained show that the toxicity of degradation by-products largely depends on the process used. With the UV/H$_2$O$_2$ system, the toxicity of degradation by-products was much higher than that of the original compound, reaching 100% bacteria inhibition after 30 min of treatment. In contrast, the degradation by-products were less toxic than the original compound with the UV/S$_2$O$_8^{2-}$ process.

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1. Introduction

Dyes are widely used in the textile, paper, food, cosmetic, and pharmaceutical industries to color their products. There are currently around 10,000 dyes available and an average of 7×10^5 tons are produced a year [1]. The textile industry is the main generator of waste with high concentrations of this type of compound, due to the large amount of water used in dying processes. Most of the dyes used in industry are synthetic and have complex aromatic structures that are resistant to biological treatment methods, leading to the persistence of these molecules in water systems for long time periods [1]. Moreover, the main problem associated with dyes are their degradation by-products, which can include a large variety of substituents in aromatic structures (e.g., amines) with a high potential to develop different types of cancer [2,3].

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Different water treatment methods have been satisfactorily applied to remove dyes, such as adsorption [4], coagulation [5], filtration [6], reverse osmosis [7], ion exchange [8], and ultrafiltration [9]. Although these methods are versatile and easy to operate, their drawback is that they are non-destructive methods that only transfer the pollutant from one phase to another, causing a secondary problem.

Over the past few years, advanced oxidation processes (AOPs) have been successfully used to degrade dyes in aqueous solution. These methods are based on generating species with high oxidizing power, such as HO· radicals, which interact with the organic molecule and degrade it into by-products with lower molecular weight or mineralizing it into CO_2 and H_2O [10,11]. Among the AOPs that have been applied to remove dyes, we highlight the Fenton and photofenton processes [1,12], ultrasound [13], ozonation [14], UV/H_2O_2 [10,12,15–25], radiolysis [26], oxidation at supercritical conditions [17], and photocatalysis [16,27]. The combined use of ultraviolet (UV) radiation and hydrogen peroxide (UV/H_2O_2) is the most widely used AOP in wastewater treatment plants.

Decolorization kinetics of various dyes using OH· radicals has been widely studied in the literature [28,29]. Haji et al. [28] investigated the degradation of methyl orange (MO) by the UV/H_2O_2 system, determining the influence of operational variables (initial dye concentration, H_2O_2 concentration, exposure area, and irradiation power). Results revealed that the dye was completely decolorized in distilled water during the first 3 min of treatment with $[MO]_0 = 7.8 \times 10^{-5}$ M and $[H_2O_2]_0 = 4.58 \times 10^{-2}$ M. Georgiou et al. [10] studied the degradation of yellow E-3GA (difluorclorpyrimidine), Revafix blue EBNA (difluorclorpyrimidine vinyl sulphonyl), RR (Vinylsulphonyl mohalogentriazine), and Remazol black B (Vinylsuyphonil x2) by the UV/H_2O_2 system. Experiments were conducted using an initial dye concentration of 100 mg/L and $[H_2O_2]_0 = 1000$ mg/L. Outcomes showed that complete decolorization was achieved with each of the dyes in deionized water within 30 min. Furthermore, at 120 min of treatment, the total organic carbon (TOC) concentration was reduced by between 80% and 100%. Similar experiments were conducted using water collected from a textile plant, revealing that complete decolorization was obtained in double the treatment time. Alternatively, it is also possible to use another type of radical species to degrade dyes, i.e., $SO_4^{-·}$, which has proven more effective than the HO· radical to remove some pharmaceutical compounds and surfactants. $SO_4^{-·}$ radicals can be produced by photolysis of the peroxodisulfate anion, with a high quantum performance, and also by chemical activation [30–33].

Few studies have analyzed dye removal by using $SO_4^{-·}$ radicals. Yeber et al. [34] studied the degradation of 100 mg/L dye Cibacron Brilliant Yellow 3 with $SO_4^{-·}$ radicals in ultrapure water, achieving 98% degradation and 90% TOC decrease after 60 min of treatment. Xu and Li [35] analyzed the degradation of dye Orange G in ultrapure water with the $S_2O_8^{2-}/Fe^{2+}$ system, studying the effect of pH, peroxodisulfate and Fe^{+2} dose, temperature, and the presence of inorganic ions (Cl^-, NO_3^-, HCO_3^-, and $H_2PO_4^-$). Results revealed that 99% degradation was obtained within 30 min of treatment and that the optimal conditions were $[S_2O_8^{2-}] = 4$ mM, $[Fe^{2+}] = 4$ mM, and pH 3.5.

With this background, the objective of the present study was to determine the effectiveness of oxidation processes based on the use of UV radiation (UV, UV/H_2O_2, and $UV/K_2S_2O_8$) in the degradation and mineralization of the remazol red (RR) dye in aqueous solution comparing the efficiency of both HO· and $SO_4^{-·}$ radicals in the degradation of this dye. The key aspects analyzed in this study are: the effect of operational variables (initial RR concentration, pH, H_2O_2 concentration, $K_2S_2O_8$ concentration, temperature, and chemical composition of waters), the TOC time course, and the toxicity of degradation by-products during the photodegradation. Remazol red was selected as parent compound because (i) it

is a colorant widely used in the textile industry and (ii) it is a non biodegradable compound.

2. Materials and methods

2.1. Reagents

The remazol red (RR) dye used in this study was obtained from a textile company with no type of purification. The reagents (analytical quality) used in this study (hydrogen peroxide, potassium peroxodisulfate, hydrochloric acid, and sodium hydroxide) were supplied by Sigma–Aldrich. Ultrapure water was obtained from Milli-Q® equipment (Millipore).

2.2. Experimental system

Remazol red degradation experiments were conducted in a photoreactor formed of concentric tubes: a stainless steel outer tube (inner diameter [i.d.] of 13 cm × height of 30 cm) and quartz inner tube (i.d. of 5.5 cm × height of 45 cm). The inner tube is equipped with a waterproof 15-Watt low-pressure mercury lamp (TNN 15/32). The annular space between the lamp and inner wall of the tube contains a sample holder with capacity for six quartz reaction tubes (i.d. of 1.5 cm × height of 20 cm). The rate of energy irradiated by the lamp was determined by actimometry, using a solution of 5 µM atrazine as actinometer and obtaining an energy of 1.027×10^{-4} Einstein s^{-1} m^{-2} for the lamp used. Solutions in reaction tubes were maintained at constant temperature by using a Frigiterm ultrathermostat, and they were kept in agitation by means of a magnetic agitation system, which permits complete homogenization of the sample.

2.3. Dye degradation by UV, UV/H_2O_2, and $UV/K_2S_2O_8$ systems

Experimental dye photodegradation data were obtained as follows: a concentrated (1000 mg/L) RR solution was prepared by adding 1 g RR to a 1 L volumetric flask and filling with ultrapure water. An aliquot (29.1–24 mL) of ultrapure water was placed in the reaction tubes, and an aliquot (0.6–3 mL) of concentrated RR solution and an aliquot (0.3–3 mL) of oxidizing agent were added to obtain a total volume of 30 mL with the desired initial concentration. RR degradation kinetics were monitored by drawing 1-mL samples at regular time intervals to determine the RR concentration, TOC, and toxicity of photodegradation by-products.

The influence of the chemical composition of water on dye photodegradation was studied by using natural waters (river surface water and urban treated wastewater) from Motril (Granada, Spain). The waters collected were filtered (0.2 µm) and storage at 277 K until use. Experiments with these waters were conducted as reported above but replacing ultrapure water with surface water or wastewater. Table 1 lists the characteristics of the natural waters used in this study.

2.4. Analytical methods

2.4.1. Dye determination in aqueous solution

The RR concentration in aqueous solution was determined by UV–Visible spectroscopy using a spectrophotometer (Spectronic Genesys 5), measuring the absorbance of RR in solution at a wavelength of 520 nm. The RR concentration was estimated from a calibration curve (absorbance *vs.* concentration).

2.4.2. TOC determination

TOC present in the sample was determined by using Shimadzu V-CSH analyzer with ASI-V autosampler,

Table 1
Chemical characteristics of the waters used.

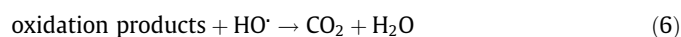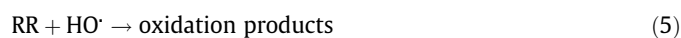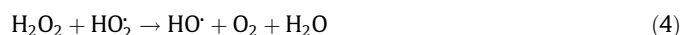| Type of water	pH	HCO_3^- (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	TOC (mg/L)	%T^a
Ultrapure	6.9	0.0	0.0	0.0	0.0	0.0	100
Surface water	8.1	3.6	1.7	59.8	4.3	38.3	92
Wastewater	7.8	9.2	3.6	88.9	6.00	103.1	50.3

[a] Transmitance.

2.4.3. Determination of the toxicity of degradation by-products

Assessment of the toxicity of degradation by-products was based on the normalized biotest (UNE/EN/ISO 11348-2) of luminescent inhibition of *Vibrio Fischeri* bacteria (NRRL B-11177), using the LUMIStox 300 system (Dr. LangeGmbH), with a LUMIStherm incubator. Toxicity is expressed as percentage inhibition at 15 min of exposure with reference to an established saline solution (control).

3. Results and discussion

3.1. UV/H$_2$O$_2$ system

RR degradation was studied by obtaining its decolorization kinetics in three systems: (i) direct photolysis with UV radiation, (ii) oxidation with H_2O_2, and (iii) oxidation with the UV/H_2O_2 system. Results (not shown) indicated that: (i) RR degradation with UV light after 60 min of exposure was 2.5%, showing that this molecule is highly resistant to degradation by direct photolysis, which is attributed to the low effectiveness of this molecule to absorb UV light at 254 nm; (ii) oxidation with H_2O_2 was also ineffective to decolorize RR (2% after 60 min of treatment), which is due to the low oxidation power of H_2O_2 and its low selectivity, and (iii) the combined system UV/H_2O_2 markedly improved the decolorization percentage of RR, achieving 100% decolorization after 60 min of treatment, attributable to the generation of HO· radicals (E_0 = 2.80 V) by the photolysis of H_2O_2. Thus, by using this last system, dye degradation took place *via* the oxidative pathway by the following reactions [19]:

$$H_2O_2 + h\nu \rightarrow 2HO^· \tag{1}$$

$$H_2O_2 + HO^· \rightarrow HO_2^· + H_2O \tag{2}$$

$$2HO_2^· \rightarrow H_2O_2 + O_2 \tag{3}$$

$$H_2O_2 + HO_2^· \rightarrow HO^· + O_2 + H_2O \tag{4}$$

$$RR + HO^· \rightarrow oxidation\ products \tag{5}$$

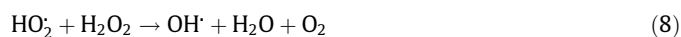$$oxidation\ products + HO^· \rightarrow CO_2 + H_2O \tag{6}$$

3.1.1. Effect of H$_2$O$_2$ concentration

The concentration of hydrogen peroxide is an important parameter that directly affects water decolorization by the UV/H_2O_2 system. Given the low molar adsorption coefficient of H_2O_2 at 254 nm (18.6–19.6 L mol^{-1} cm^{-1}), it is necessary to add an excess of H_2O_2 to produce a sufficient amount of HO· radicals. Moreover, numerous authors have reported that adding different concentrations of H_2O_2 may improve or worsen the decolorization process due to the recombination of HO· radicals at high H_2O_2 concentrations. Consequently, the optimal concentration of H_2O_2 must be determined [10].

The effect of adding H_2O_2 to the medium was assessed by performing experiments at an initial concentration of 50 mg/L RR and using initial H_2O_2 concentrations in the interval 0–15,000 µM.

Table 2 reports the experimental conditions. Fig. S1 (Supplementary information) depicts the results obtained and clearly shows that adding initial H_2O_2 concentrations of 100, 500, 1000, 5000, and 10,000 µM proportionally increased the percentage decolorization. However, this behavior was not observed when high H_2O_2 concentrations (12,500 and 15,000 µM) were added, because the experimental data under these conditions overlapped with those obtained at a H_2O_2 concentration of 10,000 µM. These results suggest that: (i) at high concentrations, H_2O_2 acts as HO· radical inhibitor by reactions (7)–(10), decreasing its effectiveness to degrade the dye [36,37], and (ii) HO· radicals, due to their low selectivity, may react mainly with degradation by-products, thereby decreasing the number of HO· radicals that can attack the original molecule.

$$HO^· + H_2O_2 \rightarrow H_2O + HO_2^· \tag{7}$$

$$HO_2^· + H_2O_2 \rightarrow OH^· + H_2O + O_2 \tag{8}$$

$$2HO_2^· \rightarrow H_2O_2 + O_2 \tag{9}$$

$$HO_2^· + HO^· \rightarrow H_2O + O_2 \tag{10}$$

Decolorization kinetics were interpreted by means of a pseudo-first order kinetic model, represented by the following equation [23]:

$$\frac{d[C_A/C_{A0}]}{dt} = -k_{Ap}[C_A/C_{A0}] \tag{11}$$

where C_A, and C_{A0} represent the concentration at time t and initial dye concentration in mg/L, respectively, and k_{AP} is the apparent rate constant in min^{-1}. Table 2 lists the values of k_{AP} and R^2 and shows that the pseudo-first order kinetic model interpreted experimental data reasonably well, given that R^2 values were close to unity in most experiments.

A key aspect of the effectiveness of the UV/H_2O_2 system is the degree of mineralization of the organic matter present in the medium, which was assessed by obtaining the TOC content variation as a function of time. Table 2 exhibits the percentage TOC reduction after 60 min of treatment (TOC$_{60}$), showing that the rise in H_2O_2 concentration produced a linear increase in percentage TOC$_{60}$ reduction. These results show that, although decolorization kinetics were not accelerated at high H_2O_2 concentrations, there was an increase in the percentage organic matter mineralization, verifying that HO· radicals have a low selectivity at high concentrations and mainly react with the degradation by-products rather than with the original compound.

3.1.2. Effect of initial dye concentration

The effect of the initial dye concentration on the decolorization kinetics was determined by conducting experiments at 20, 50, and 100 mg/L with an initial H_2O_2 concentration of 1000 µM. Fig. S2 (Supplementary information) depicts the results obtained, showing that the decolorization process becomes slower with higher dye concentrations; thus, 99.9%, 81.0%, and 47.7% decolorization was obtained after 60 min when using initial concentrations of 20, 50, and 100 mg/L, respectively, which is mainly due to: (i) a

Table 2
Experimental conditions, apparent reaction rate constants, and percentage decolorization and mineralization values for RR degradation by UV/H_2O_2.

Exp no.	Water Type	$[RR]_0$ (mg/L)	T (K)	$[H_2O_2]_0$ (μM)	pH_i	pH_f	k_{AP} (min^{-1})	R^2	$\%D_{60}$	$\%TOC_{60}$
1	UW	50	298	0	6.94	6.92	$4.22 \pm 0.02 \times 10^{-4}$	0.9999	2.50	0.08
2	UW	50	298	100	6.19	5.71	$3.00 \pm 0.06 \times 10^{-3}$	0.9999	16.49	7.46
3	UW	50	298	500	6.13	4.62	$1.09 \pm 0.02 \times 10^{-2}$	0.9961	47.94	16.21
4	UW	50	298	1000	6.76	4.18	$1.88 \pm 0.03 \times 10^{-2}$	0.9997	67.63	21.03
5	UW	50	298	5000	6.31	4.01	$4.94 \pm 0.09 \times 10^{-2}$	0.9994	94.85	29.41
6	UW	50	298	10,000	5.35	3.09	$1.51 \pm 0.03 \times 10^{-1}$	0.9996	99.99	37.42
7	UW	50	298	12,500	5.90	3.85	$1.47 \pm 0.06 \times 10^{-1}$	0.9919	99.99	64.93
8	UW	50	298	15,000	5.88	3.68	$1.57 \pm 0.07 \times 10^{-1}$	0.9907	99.99	74.76
9	UW	50	298	1000	3.02	3.01	$3.29 \pm 0.26 \times 10^{-2}$	0.9873	86.15	20.71
10	UW	50	298	1000	10.99	10.18	$1.94 \pm 0.09 \times 10^{-2}$	0.9972	68.72	10.00
11	UW	20	298	1000	6.86	5.38	$1.49 \pm 0.11 \times 10^{-1}$	0.9851	99.99	20.18
12	UW	100	298	1000	6.90	4.26	$1.08 \pm 0.01 \times 10^{-2}$	0.9999	47.66	19.89
13	UW	50	288	1000	6.75	4.29	$1.76 \pm 0.09 \times 10^{-2}$	0.9997	65.25	20.87
14	UW	50	313	1000	6.76	4.15	$4.04 \pm 0.09 \times 10^{-2}$	0.9991	91.14	23.49
15	WW	50	298	100	8.19	7.99	$1.90 \pm 0.17 \times 10^{-3}$	0.9998	10.77	1.35
16	WW	50	298	500	8.28	8.20	$5.37 \pm 0.25 \times 10^{-3}$	0.9996	27.53	3.37
17	WW	50	298	1000	8.31	8.26	$7.77 \pm 0.21 \times 10^{-3}$	0.9997	37.26	8.18
18	WW	50	298	5000	8.56	7.73	$1.30 \pm 0.06 \times 10^{-2}$	0.9998	54.26	10.89
19	WW	50	298	10,000	7.95	7.42	$7.59 \pm 0.11 \times 10^{-2}$	0.9997	98.95	17.20
20	SW	50	298	100	8.28	8.27	$1.99 \pm 0.11 \times 10^{-3}$	0.9999	11.24	3.61
21	SW	50	298	500	8.07	7.84	$1.21 \pm 0.08 \times 10^{-2}$	0.9973	51.49	4.37
22	SW	50	298	1000	8.10	7.72	$1.45 \pm 0.06 \times 10^{-2}$	0.9982	57.98	12.11
23	SW	50	298	5000	8.36	7.43	$1.93 \pm 0.02 \times 10^{-2}$	0.9981	68.68	13.61
24	SW	50	298	10,000	8.14	7.15	$1.09 \pm 0.05 \times 10^{-1}$	0.9978	98.85	17.90

decrease in the $[HO^\cdot]/[RR]_0$ ratio and (ii) a decrease in light penetration with higher initial dye concentrations, which reduces the $HO^\cdot$ radical formation rate. Table 2 shows the k_{AP} and R^2 values of these experiments. Table 2 also reports the TOC_{60} reduction at the three initial dye concentrations, showing a gradual rise in this value with higher initial concentrations. Higher dye concentrations produced a greater number of degradation by-products competing with the original molecule for the reactive species of the medium, thereby reducing the decolorization rate but increasing the degree of organic matter mineralization.

3.1.3. Effect of solution pH

The effect of pH on dye degradation was studied by conducting experiments at pH 3, 7, and 11. Results obtained (Fig. S3, Supplementary information) show that the maximum dye degradation rate was obtained at acid pH ($k_{AP} = 3.29 \times 10^{-2}$ min^{-1}), decreased with a pH rise from 3 to 7, and remained constant at pH 7 to 11. These results can be explained by considering that H_2O_2 reactivity strongly depends on the medium pH, given that a basic pH favors its decomposition into water and molecular oxygen instead of $HO^\cdot$. Furthermore, under alkaline conditions, the conjugated base of hydrogen peroxide (HO_2^-) is produced (reaction 12), which acts as scavenger of $HO^\cdot$ radicals in the medium according to reactions (13)–(16).

$$H_2O_2 + OH^- \rightarrow HO_2^- + H_2O \tag{12}$$

$$HO_2^- + HO^\cdot \rightarrow H_2O + O_2^- \tag{13}$$

$$O_2^- + HO^\cdot \rightarrow O_2 + OH^- \tag{14}$$

$$OH^\cdot + OH^- \rightarrow O^{\cdot-} + H_2O \tag{15}$$

$$O^{\cdot-} + O_2^- + H_2O \rightarrow 2OH^- + O_2 \tag{16}$$

Dye mineralization at different pH values showed a very similar effect to that obtained for degradation kinetics, observing the highest percentage mineralization at pH 3 (20%) and the lowest at pH

11 (10%). These results verify that basic pH values promote the recombination of $HO^\cdot$ radicals, reducing the decolorization rate and percentage organic matter mineralization.
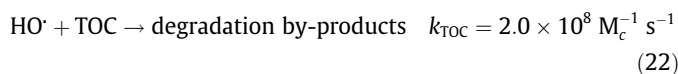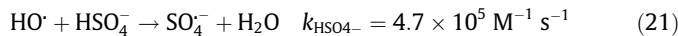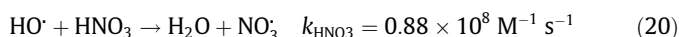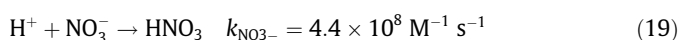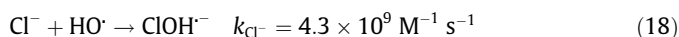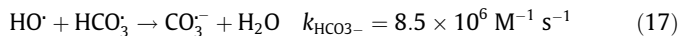
3.1.4. Effect of temperature

The effect of temperature was analyzed by conducting experiments in a temperature range of 288–313 K, using an initial dye concentration of 50 mg/L and H_2O_2 concentration of 1000 μM at pH $\approx$ 7. Results obtained (Fig. S4, Supplementary information) show that the degradation kinetics at 288 and 298 K were very similar, achieving 66% decolorization at both temperatures after 60 min of treatment. This figure also shows that the decolorization kinetics were improved by increasing the system temperature from 298 to 313 K, thus, after 60 min of treatment, 91% decolorization was achieved at 313 K. These results can be explained by considering that high temperatures favor the decomposition of H_2O_2. Lee et al. [38] studied the decomposition of H_2O_2 at different temperatures and found that the decomposition rate was only slightly affected in the temperature range from 281 to 303 K and exponentially increased from 303 to 323 K. Moreover, in most chemical reactions, a temperature increase produces an increase in the reaction rate constant, accelerating the generation of radical species and their reaction with the molecules in the medium.

Temperature changes in the range used did not have a major effect on the mineralization of RR degradation by-products, and similar percentage mineralization values were obtained at all temperatures studied, indicating that temperature largely favors the main reaction between $HO^\cdot$ radicals and the RR molecules and considerably reduces the amount of radical species in the medium for the continued degradation of by-products into CO_2 and water.

3.1.5. Degradation of RR in natural waters

The applicability of the UV/H_2O_2 system for the removal of RR was tested in natural waters with different chemical compositions (Table 1). Fig. 1 depicts the variation in percentage decolorization in the three types of water at different initial H_2O_2 concentrations,

showing that there was generally a reduction in the percentage removal and, therefore, in the apparent rate constant of RR degradation in surface water and wastewater at H_2O_2 concentrations <10,000 μM. The decolorization kinetics in wastewater showed the lowest apparent reaction rate constant, largely attributable to the lower transmittance in this type of water ($T = 50.3$), which reduces the absorption of UV radiation and therefore the number of photons that can interact with H_2O_2 to generate HO· radicals. The lower percentage decolorization in surface and waste waters can be attributed to HO· radical inhibition due to the presence of bicarbonates, chlorides, sulfates, nitrates, and inorganic matter in natural waters. Eqs. (17)–(22) summarize the main reactions between these species and the OH· radical [39,40].

$$HO^· + HCO_3^- \rightarrow CO_3^{·-} + H_2O \quad k_{HCO3-} = 8.5 \times 10^6 \ M^{-1} \ s^{-1} \tag{17}$$

$$Cl^- + HO^· \rightarrow ClOH^{·-} \quad k_{Cl^-} = 4.3 \times 10^9 \ M^{-1} \ s^{-1} \tag{18}$$

$$H^+ + NO_3^- \rightarrow HNO_3 \quad k_{NO3-} = 4.4 \times 10^8 \ M^{-1} \ s^{-1} \tag{19}$$

$$HO^· + HNO_3 \rightarrow H_2O + NO_3^· \quad k_{HNO3} = 0.88 \times 10^8 \ M^{-1} \ s^{-1} \tag{20}$$

Fig. 1. Effect of the type of water on the percentage decolorization by the UV/H_2O_2 system. [RR]$_0$ = 50 mg/L, T = 298 K, [H_2O_2]$_0$ = 1000 μM, pH = 7. (A) Ultrapure water, (B) surface water, and (C) urban treated waste water.

$$HO^· + HSO_4^- \rightarrow SO_4^{·-} + H_2O \quad k_{HSO4-} = 4.7 \times 10^5 \ M^{-1} \ s^{-1} \tag{21}$$

$$HO^· + TOC \rightarrow degradation \ by\text{-}products \quad k_{TOC} = 2.0 \times 10^8 \ M_c^{-1} \ s^{-1} \tag{22}$$

The inhibition rate of HO· radicals due to the presence of Cl^-, HCO_3^-, NO_3^-, SO_4^{2-}, TOC, and H^+ was determined by the following equation:

$$r_{OH^·} = k_{HCO_3^-} - [HCO_3^-] + k_{Cl^-}[Cl^-] + k_{H^+}[H^+] + k_{SO_4^{2-}}[SO_4^{2-}]$$
$$+ k_{NO_3^-}[NO_3^-] + k_{TOC}[TOC] \tag{23}$$

The HO· radical inhibition rate determined for surface and waste waters was $r_{OH^·} = 8.52 \times 10^5 \ s^{-1}$ and $r_{OH^·} = 2.17 \times 10^6 \ s^{-1}$, respectively. These results indicate the HO· radical inhibition rate is 2.54-fold higher in wastewater than in surface water, explaining why this type of water yielded the lowest percentage decolorization.

Fig. 2 depicts the percentage mineralization obtained in the three types of water after 60 min of treatment with different initial H_2O_2 concentrations, showing that the highest percentage mineralization was obtained in ultrapure water, followed by surface and waste water. However, in absolute terms and considering the large amount of organic matter present in surface water (38.30 mg/L) and wastewater (103.13 mg/L), the highest reduction in organic matter was in the presence of wastewater, followed by surface water and ultrapure water. These results verify that the decrease in decolorization kinetics in wastewater is mainly due to competition of the RR molecules and organic matter for the HO· radicals in the medium.

3.2. UV/$S_2O_8^{2-}$ system

Peroxodisulfate ($S_2O_8^{2-}$) is a strong oxidant (E_0 = 2.05 V) used in the petroleum industry to treat hydraulic fluids or as reaction initiator [41]); it is also used to degrade some organic pollutants. However, given that reactions with $S_2O_8^{2-}$ are very slow at ambient temperature, various methods have been proposed to activate or accelerate the decomposition of organic molecules [42]. The most frequently used activation methods generate sulfate radicals $SO_4^{·-}$ (E_0 = 2.6 V) by the photochemical, thermal, or chemical decomposition of $S_2O_8^{2-}$ [43–45]. Eqs. (24)–(35) show the simplified reactions in the photochemical activation of $S_2O_8^{2-}$ [42].
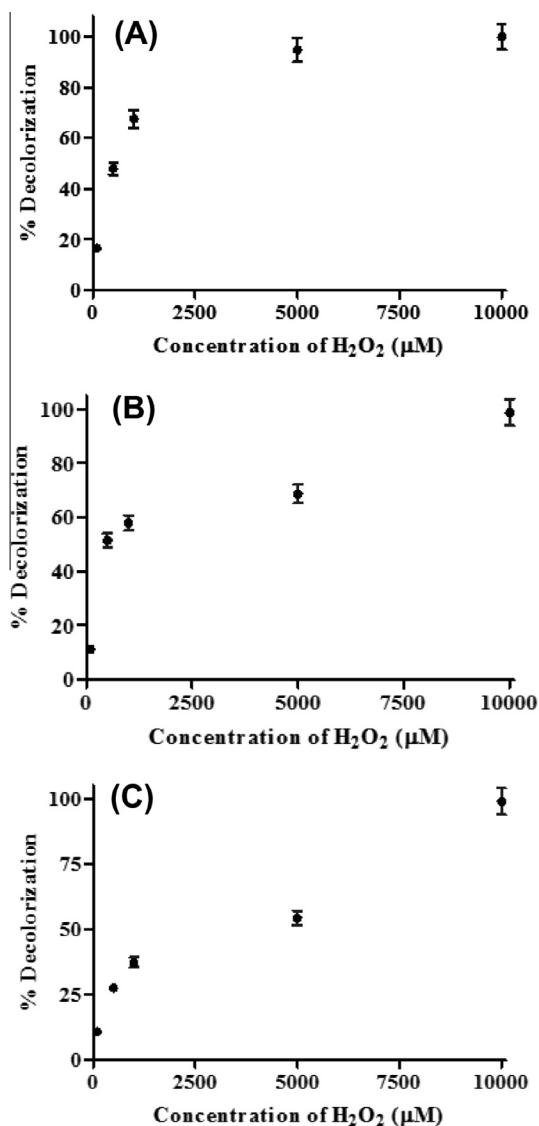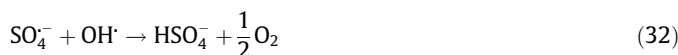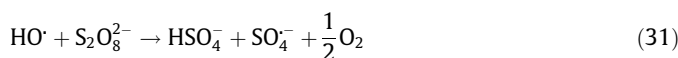
$$S_2O_8^{2-} + h\nu \rightarrow 2SO_4^{·-} \tag{24}$$

$$SO_4^{·-} + RH_2 \rightarrow SO_4^{2-} + H^+ + RH^· \tag{25}$$

$$RH^· + S_2O_8^{2-} \rightarrow R + SO_4^{2-} + H^+ + SO_4^{·-} \tag{26}$$

$$SO_4^{·-} + RH \rightarrow R^· + SO_4^{2-} + H^+ \tag{27}$$

$$2R^· \rightarrow RR \ (dimer) \tag{28}$$

$$SO_4^{·-} + H_2O \rightarrow HSO_4^- + HO^· \tag{29}$$

$$HSO_4^- \rightarrow H^+ + SO_4^{2-} \tag{30}$$

$$HO^· + S_2O_8^{2-} \rightarrow HSO_4^- + SO_4^{·-} + \frac{1}{2}O_2 \tag{31}$$

$$SO_4^{·-} + OH^· \rightarrow HSO_4^- + \frac{1}{2}O_2 \tag{32}$$
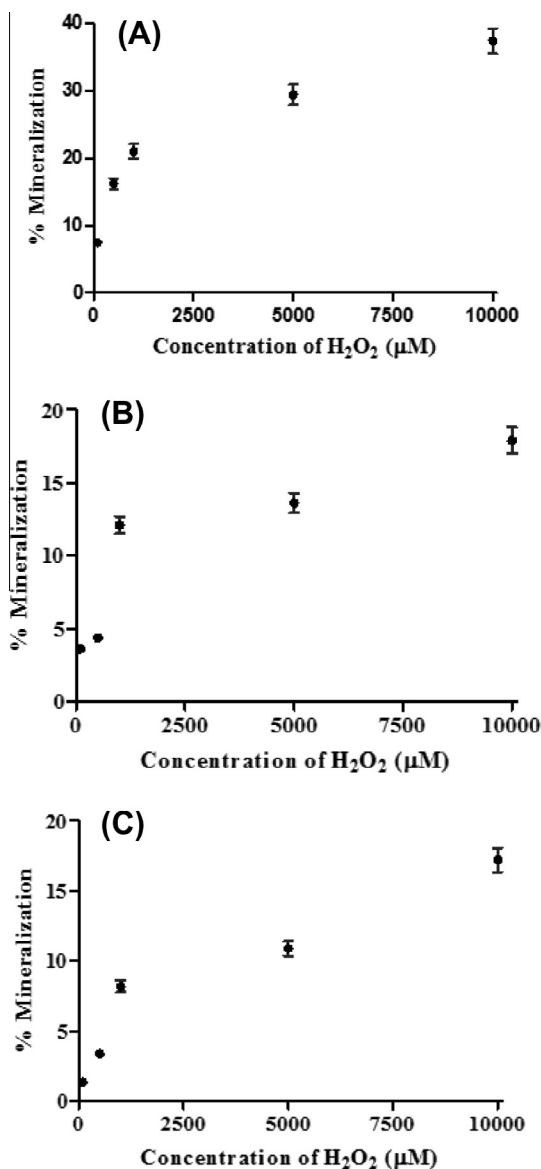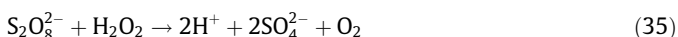
$$2OH^· \rightarrow 2H_2O_2 \tag{33}$$

Fig. 2. Effect of the type of water on the percentage mineralization of organic matter with the UV/H_2O_2 system. $[RR]_0 = 50$ mg/L, $T = 298$ K, $[H_2O_2]_0 = 1000$ μM, pH = 7. (A) Ultrapure water, (B) surface water, and (C) urban treated waste water.

$$HO^· + H_2O_2 \rightarrow H_2O + HO_2^· \tag{34}$$

$$S_2O_8^{2-} + H_2O_2 \rightarrow 2H^+ + 2SO_4^{2-} + O_2 \tag{35}$$

The above reactions show that the oxidation process begins with the formation of sulfate and hydroxyl radicals, which can transform organic matter into more or less toxic by-products or into CO_2 and H_2O.

Fig. S5 (Supplementary information) depicts RR degradation with the $S_2O_8^{2-}$ and UV/$S_2O_8^{2-}$ systems, clearly showing that peroxodisulfate only achieves 1% decolorization, whereas the presence of UV light accelerates RR decomposition due to the generation of highly reactive species, such as $SO_4^·{}^-$ and $HO^·$ radicals.

3.2.1. Effect of initial $S_2O_8^{2-}$ concentration

In order to elucidate and compare the effectiveness of the UV/$S_2O_8^{2-}$ system and the UV/H_2O_2 system to decolorize and mineralize RR solutions, experiments were conducted at different

$S_2O_8^{2-}$ concentrations using the same initial RR concentration. These initial $S_2O_8^{2-}$ concentrations were the same as those used with the UV/H_2O_2 system, i.e., from 100 to 15,000 μM. Fig. S6 (Supplementary information) depicts the decolorization kinetics at different initial $S_2O_8^{2-}$ concentrations, showing that the addition of $K_2S_2O_8$ produces a major increase in the degradation rate with a rise in the initial $S_2O_8^{2-}$ concentration, obtaining 90% RR degradation after 60 min of treatment with the addition of 1000 μM $K_2S_2O_8$. 100% decolorization was achieved in 10 min when concentrations >1000 μM were used. We can also observe that for these same conditions, the percentage decolorization was higher than achieved with the UV/H_2O_2 system (Table 2).

Experimental data were fitted by using Eq. (2), and Table 3 shows the apparent reaction rate constants obtained. Comparison of these results with those for the UV/H_2O_2 system (Table 2) show that, under the above-reported experimental conditions, the apparent reaction rate constants were around 2.5-fold higher with the $K_2S_2O_8$ system. Furthermore, a linear increase in k_{AP} was observed with higher initial $S_2O_8^{2-}$ concentrations using the UV/$S_2O_8^{2-}$ system, whereas the k_{AP} value remained constant with the UV/H_2O_2 system. These results indicate a greater selectivity of $SO_4^·{}^-$ radicals to degrade the RR molecule in comparison to $HO^·$ radicals.

Table 3 shows that the percentage mineralization of organic matter with the UV/$S_2O_8^{2-}$ system drastically increased until reaching 97% TOC reduction at an initial $S_2O_8^{2-}$ concentration of 15,000 μM, a much higher reduction than was obtained under the same conditions with the UV/H_2O_2 system (74%). These results confirm that $SO_4^·{}^-$ radicals are more effective to degrade RR and its degradation by-products than are $HO^·$ radicals, attributable to their almost 10-fold slower recombination rate ($k_{SO4}^· = 4 \times 10^8$ M^{-1} s^{-1}) in comparison to $HO^·$ radicals ($k_{OH}^· = 5.5 \times 10^9$ M^{-1} s^{-1}).

3.2.2. Effect of initial dye concentration

The effect of the initial RR concentration was studied by conducting experiments at different initial RR concentrations (20, 50, and 100 mg/L) but the same initial $K_2S_2O_8$ concentration (1000 μM) (Table 3, Exp. No. 4, 11–12). Fig. S7 (Supplementary information) depicts the decolorization kinetics obtained and shows that, as with the UV/H_2O_2 system, the degradation kinetics become much faster with lower RR concentrations. However, the UV/$K_2S_2O_8$ system is much more effective than the UV/H_2O_2 system with both high and low RR concentrations and yields higher k_{AP} values. Additionally, the percentage TOC_{60} reduction values were also higher with the UV/$K_2S_2O_8$ system.

3.2.3. Effect of solution pH

The results in Fig. S8 (Supplementary information) and Table 3 [Exp. Nos. 4, 8–9] show that RR degradation is slightly favored by increased pH values, as indicated by the apparent rate constants. After 60 min of treatment, the percentage degradation values at pH 3, 7, and 10, were 86%, 90%, and 92%, respectively. The TOC_{60} reduction was very similar at all three pH values, obtaining around 10% mineralization of the organic matter present in the sample. The percentage TOC_{60} mineralization was similar between the H_2O_2 and $S_2O_8^{2-}$ systems, although the solution decolorization was greater in the latter.

3.2.4. Effect of temperature

Fig. S9 (Supplementary information) depicts the effect of temperature on RR decolorization kinetics with the UV/$S_2O_8^{2-}$ system. In contrast to the UV/H_2O_2 system, there was a clear tendency towards a linear increase in k_{AP} values with rising temperatures, with a percentage decolorization of 81.5%, 90%, and 99.84% at temperatures of 288, 298, and 313 K, respectively. The rate constants obtained with the UV/$S_2O_8^{2-}$ system were 2.81×10^{-2},

Table 3
Experimental conditions, apparent reaction rate constants, decolorization and percentage mineralization for RR degradation with $UV/K_2S_2O_8$.

Exp No.	Water Type	$[RR]_0$ (mg/L)	T (K)	$[S_2O_8^{2-}]_0$ (μM)	pH_i	pH_f	k_{AP} (min^{-1})	R^2	$D_{60}\%$	$TOC_{60}\%$
1	UW	50	298	0	6.94	6.92	$4.22 \pm 0.16 \times 10^{-4}$	0.9999	2.50	0.08
2	UW	50	298	100	6.72	4.88	$3.20 \pm 0.12 \times 10^{-3}$	0.9999	17.47	6.91
3	UW	50	298	500	6.89	4.01	$2.05 \pm 0.08 \times 10^{-2}$	0.9978	70.74	8.05
4	UW	50	298	1000	6.82	3.17	$3.81 \pm 0.07 \times 10^{-2}$	0.9991	89.86	9.13
5	UW	50	298	5000	6.62	2.86	$1.41 \pm 0.01 \times 10^{-1}$	0.9998	99.98	32.08
6	UW	50	298	10000	6.68	2.60	$3.22 \pm 0.60 \times 10^{-1}$	0.9965	100.00	41.79
7	UW	50	298	12500	6.63	2.43	$4.74 \pm 0.24 \times 10^{-1}$	0.9938	100.00	92.82
8	UW	50	298	15000	6.74	2.33	$5.40 \pm 0.25 \times 10^{-1}$	0.9951	100.00	97.05
9	UW	50	298	1000	3.02	2.92	$3.22 \pm 0.28 \times 10^{-2}$	0.9851	85.50	10.39
10	UW	50	298	1000	10.45	10.20	$4.12 \pm 0.56 \times 10^{-2}$	0.9919	91.54	10.31
11	UW	20	298	1000	6.78	5.13	$4.12 \pm 0.41 \times 10^{-1}$	0.9863	100.00	38.97
12	UW	100	298	1000	6.76	5.42	$1.39 \pm 0.09 \times 10^{-2}$	0.9998	56.48	10.29
13	UW	50	288	1000	6.78	3.53	$2.81 \pm 0.06 \times 10^{-2}$	0.9991	81.45	8.70
14	UW	50	313	1000	6.69	3.36	$1.07 \pm 0.04 \times 10^{-1}$	0.9981	99.84	16.56
15	WW	50	298	100	8.62	8.56	$5.72 \pm 0.13 \times 10^{-4}$	0.9999	3.38	0.95
16	WW	50	298	500	8.51	8.40	$2.36 \pm 0.07 \times 10^{-3}$	0.9999	13.20	1.98
17	WW	50	298	1000	8.64	8.58	$4.69 \pm 0.06 \times 10^{-3}$	0.9999	24.55	2.61
18	WW	50	298	5000	8.62	8.24	$4.4 \pm 0.18 \times 10^{-2}$	0.9970	93.00	16.13
19	WW	50	298	10000	8.60	8.12	$1.31 \pm 0.04 \times 10^{-1}$	0.9991	99.96	18.68
20	SW	50	298	100	8.48	8.32	$1.68 \pm 0.13 \times 10^{-3}$	0.9999	9.56	1.80
21	SW	50	298	500	8.43	8.37	$5.37 \pm 0.25 \times 10^{-3}$	0.9996	27.52	2.79
22	SW	50	298	1000	8.44	8.37	$1.47 \pm 0.05 \times 10^{-2}$	0.9988	58.71	4.12
23	SW	50	298	5000	8.45	8.32	$8.85 \pm 0.12 \times 10^{-2}$	0.9997	99.50	12.65
24	SW	50	298	10000	8.27	7.39	$2.13 \pm 0.17 \times 10^{-1}$	0.9973	100.00	31.38

3.81×10^{-2}, and 7.40×10^{-2} min^{-1}, respectively, i.e., almost 2-fold higher than those obtained with the UV/H_2O_2 system. There was also a moderate increase in percentage TOC_{60} reduction with the rise in temperature; but the percentage mineralization was lower than that obtained with the UV/H_2O_2 system at all three temperatures.
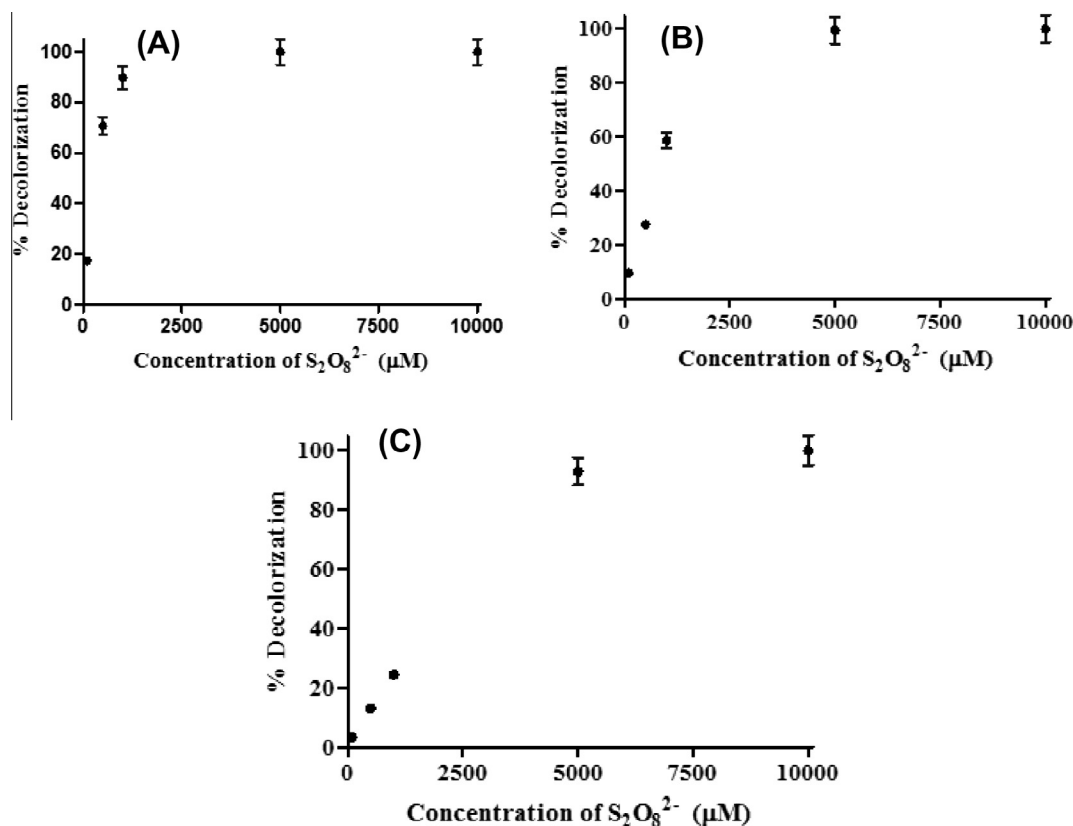

Fig. 3. Variation in the percentage decolorization as a function of the type of water and initial $S_2O_8^{2-}$ concentration. (A) Ultrapure water, (B) surface water, and (C) urban treated waste water.

3.2.5. Effect of the type of water

The results of applying the $UV/S_2O_8^{2-}$ system in natural waters are depicted in Fig. 3, which shows the percentage decolorization obtained after 60 min in the different types of water as a function of the initial $S_2O_8^{2-}$ dose. The results show that a high $S_2O_8^{2-}$ dose (10,000 μM) is required to obtain complete decolorization in the three types of water. Furthermore, at concentrations <5000 μM, the decolorization strongly depends on the type of water, with a decrease in maximum percentage decolorization in the order ultrapure water > surface water > wastewater. Table 3 lists the decolorization rate constants of the dye, showing that the rate constant in ultrapure water was around 6-fold higher than obtained in wastewater and 2-fold higher than that in surface water, while k_{AP} values were around 2.5-fold lower in surface water than in wastewater. As commented above, this may be attributable to a screening effect of the dissolved organic matter, which absorbs part of the UV radiation, and to the inhibition of oxidizing species in wastewater.

According to the results shown in Tables 2 and 3, k_{AP} values were higher with the $UV/S_2O_8^{2-}$ system than with the UV/H_2O_2 system in ultrapure water but higher with the UV/H_2O_2 system than with the $UV/S_2O_8^{2-}$ system in natural waters. A similar behavior can be observed in the organic matter mineralization, given that a greater percentage TOC_{60} reduction was obtained with SO_4^{-} radicals in ultrapure water but with $OH^{\cdot}$ radicals in natural waters.

3.2.6. Time course of toxicity

One of the most important aspects of the effectiveness of a treatment system is the time course of the toxicity of degradation by-products. Although the complete mineralization of the organic matter can be obtained with both systems under study, it requires the addition of a large amount of H_2O_2 or $S_2O_8^{2-}$ or the irradiation of samples for 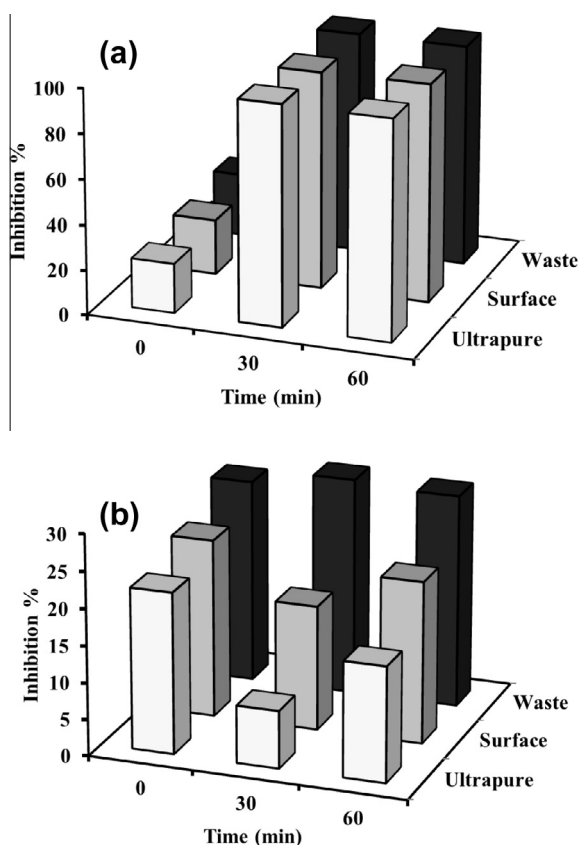long time periods, increasing the treatment costs. It is essential to determine the medium toxicity as a function of treatment time in order to ensure that by-products harmful to living beings are not generated. Fig. 4a and b depicts the toxicity values measured in the water samples after different treatment times with the UV/H_2O_2 and $UV/S_2O_8^{2-}$ systems. They show that the toxicity of degradation by-products largely depends on the system used. Thus, it was much higher than the toxicity of the original compound in all three water types with the UV/H_2O_2 system, reaching 100% bacteria inhibition after 30 min of treatment, whereas it was lower than that of the original compound with the $UV/S_2O_8^{2-}$ system, with the difference in toxicity between byproducts and original compound being highest in ultrapure water, followed by surface and waste water. These results verify that the $UV/S_2O_8^{2-}$ system is a better treatment option for removing color from natural waters.

4. Conclusions

Results obtained demonstrate UV radiation to be unable to degrade RR but the addition of H_2O_2 or $K_2S_2O_8$ to the photodegradation reactor markedly accelerates oxidation of the dye.

Apparent reaction rate constants of RR are around 2.5-fold higher with the $UV/S_2O_8^{2-}$ system than with the UV/H_2O_2 system. Sulfate radicals have a greater selectivity to degrade the RR molecule in comparison to $HO^{\cdot}$ radicals.

The k_{AP} values obtained were higher with the $UV/S_2O_8^{2-}$ system than with the UV/H_2O_2 system in ultrapure water, but an opposite behavior was observed in natural waters, in which the values were higher with the UV/H_2O_2 system than with the $UV/S_2O_8^{2-}$ system. Likewise, results for the mineralization of organic matter showed a greater reduction in TOC_{60} by SO_4^{-} radicals in ultrapure water and by $HO^{\cdot}$ radicals in natural waters.

The toxicity of degradation by-products largely depends on the system used. Thus, it was much higher than the toxicity of the original compound in all three water types with the UV/H_2O_2 system, reaching 100% bacteria inhibition in 30 min of treatment, whereas it was lower than that of the original compound with the $UV/S_2O_8^{2-}$ system, with the difference in toxicity between byproducts and original compound being highest in ultrapure water, followed by surface and waste water.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2013.02.127.

Fig. 4. Time course of toxicity in different types of water with (a) UV/H_2O_2 and (b) $UV/S_2O_8^{2-}$ systems. $[RR]_0$ = 50 ppm, T = 298 K, pH = 7.

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