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Study of photochemical and sonochemical processes efficiency for degradation of dyes in aqueous solution

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Abstract−The degradation of two commercially available dyestuffs (C.I. Reactive Black 5 and C.I. Disperse Orange 25) by ultraviolet radiation (UV), ultrasonic irradiation (US), UV/H_2O_2 and US/H_2O_2 processes was investigated in a laboratory-scale batch photoreactor equipped with a 55 W immersed-type low-pressure mercury vapor lamp and a sonoreactor with low frequency (42 kHz) plate type transducer at 170 W of acoustic power. The toxicity was also evaluated in acute toxicity studies using *Daphnia magna*. Results showed that color removal efficiencies by US and US/H_2O_2 processes were negligible for both dyes. Almost complete disappearance of Reactive Black 5 (97.9%) in UV/H_2O_2 process was possible after 5 min of irradiation. The maximum color removal efficiency of Disperse Orange 25 after 10 min of irradiation, however, was only 9.2% and reached a maximum value of 41% after 120 min of irradiation. Pseudo-first order kinetics with respect to dyestuffs concentrations was found to fit all the experimental data. The results clearly showed that both dyes examined were toxic to *D. magna* and resulted in quite low LC_{50} values.

Key words: Decolorization, Reactive Black 5, Disperse Orange 25, Advanced Oxidation Processes, Toxicity

INTRODUCTION

Colored wastewater from textile, dyeing, pulp and paper industries is a problem in large parts of the world. Due to their relatively high solubility, synthetic dyes are common water pollutants and may frequently be found in trace quantities in industrial wastewater [1]. The removal of dye from those effluents is one of the most significant environmental problems. The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and undesirable [2,3]. Hence, contaminations due to dyes pose not only a severe public health concern, but also many serious environmental problems because of their persistence in nature and nonbiodegradable characteristics [4]. Dyes may significantly affect photosynthetic activity in aquatic life because of reduced light penetration and may also be toxic to some aquatic life due to the presence of aromatics and metals, chlorides, etc. Dyes usually have a synthetic origin and complex aromatic molecular structures which make them more stable and more difficult to biodegrade [5].

Azo dyes are synthetic organic compounds widely used in textile, leather, plastic pharmaceutical, food, paint and other industries. They are characterized by the presence of at least one nitrogen to nitrogen double bonds (-N=N-) bearing aromatic rings, and dominate the worldwide market of dyestuffs with a share of about 70% [6]. Reactive azo dyes released from textile dyeing plants are highly resistant to conventional wastewater treatment processes. In fact, as much as 90% of reactive dyes could remain unaffected after activated sludge treatment [7]. Therefore, alternative methods should be implemented for effective pollution abatement of dyed effluents. Several techniques, such as electrochemical degradation [8], AOPs [9-11], AOP- biological treatment [3,5,7], and adsorption [12], have been studied for removal of azo dyes from wastewater.

In the past two decades, advanced oxidation processes (AOPs) have appeared more appropriate for treating wastewaters containing organic dyes [10,11]. AOPs are defined as the processes that involve highly reactive species, specifically hydroxyl radicals (oxidation potential 2.8 V), in sufficient quantities to oxidize the majority of complex organic chemicals in the water effluent [13,14]. Hydroxyl radicals have become the most important oxidants due to their high reactivity and lack of selectivity towards organic compounds [15]. The methods for generating these radicals are diverse, ranging from photochemistry to sonochemistry. Besides photolysis and sonolysis, utilization of Fenton process, ozonation, non-thermal plasma formed by electrical discharge and UV radiation in combination with ozone, hydrogen peroxide, or photocatalysts like TiO_2 and ZnO are also reported in the literature [15].

Sonication is a relatively innovative AOP based on the use of low to medium frequency (typically in the range 20-1,000 kHz) and high energy ultrasound to catalyze the destruction of organic pollutants in waters [16]. The chemical effects of ultrasound irradiation are the result of acoustic cavitation, which is the formation and subsequent collapse of micro-bubbles in a liquid [13,17]. When aqueous solutions are exposed to ultrasound, transient cavitations are formed due to compression and rarefaction of the bulk water. Under these extreme conditions hydroxyl radicals and hydrogen atoms are formed by opening the H-O bond [13,17]. Volatile and hydrophilic compounds react at the layer between cavitation and bulk water with the supercritical water and inside the bulk water with the ejected hydroxyl radicals, while simple volatile and hydrophobic compounds are pyrolyzed inside the cavitation bubble [17]. Sonochemical treatment typically operates at ambient conditions and does not require the addition of extra chemicals or catalysts [18].

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Another technology is photolysis. Direct photolysis has been always considered as one possible alternative because it is possible for molecules of most organic compounds to transform, to cleave bonds, and even to undergo complete destruction in the presence of ultraviolet (UV) irradiation [19,20]. According to the literature review, no study was found that decolorized the Disperse Orange 25 (DO25) and Reactive Black 5 (RB5) azo dyes using low frequency (42 kHz, 170 W) sonochemical processes and UV radiation (low-pressure, 55 W) either alone or in conjunction with hydrogen peroxide. Therefore, the main aim of this study was to investigate the application of low frequency ultrasound and low pressure mercury vapor lamp for the degradation of the two above-mentioned dyes either alone or in conjunction with hydrogen peroxide in a pilot scale reactor. The effects of the key operating parameters such as pH, initial dye concentration and hydrogen peroxide dosage on the decolorization were also studied. Another objective of the study was to determine the optimal condition for each process including the time required for complete degradation. Also, comparisons between applied processes in terms of degradation efficiency and discussion about the difference between resistances of both dyes on the basis of experimental data were remarked.

MATERIALS AND METHODS

The dyes C.I. Reactive Black 5 and C.I. Disperse Orange 25 were obtained from Alvan Sabet dye manufacturing industry located in Hamedan, Iran and used without any purification. The chemical structures of the two azo dyes are shown in Figs. 1 and 2. All other chemicals used in the experiments were obtained from Merck Chemical Co, Iran. All model solutions of dyes were prepared using deionized water with the initial concentration of 10-50 mg L^{-1}. In each case, the reaction volume was 2,500 ml. The pH of each tested solution was adjusted to the required value with concentrated H_2SO_4 and NaOH solution. No pH monitoring was accomplished during the reactions. Sonication was achieved at a frequency of 42 kHz (170 W) with an ultrasonic generator (Codyson CD-4820, China) with a piezoelectric transducer having a diameter of 5 cm fixed at the bottom of the vessel (Fig. 3). Ultrasonic energy dissipated in the reactor was set at 60 W. The apparatus was open to air. The sonochemical reactions were carried out for 180 min. The photodegradation studies were carried out in a batch reactor system. The photoreactor consisted of a 2,500 ml cylindrical stainless steel body. A 55 W low pressure mercury lamp (I=50,000 μW cm^{-2}, 909 mm long) surrounded by quartz jacket was located in the center of the reactor (Fig. 4). The photolysis reactions were carried out for 120 min. Samples were taken periodically from the reactors and analyzed immediately. The temperature of the reactors contents was maintained at

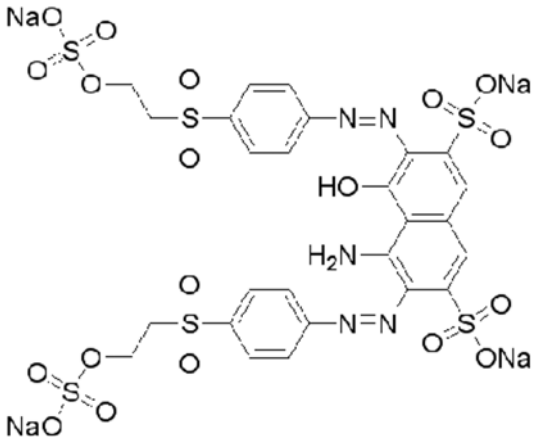

Fig. 1. Chemical structure of RB5.

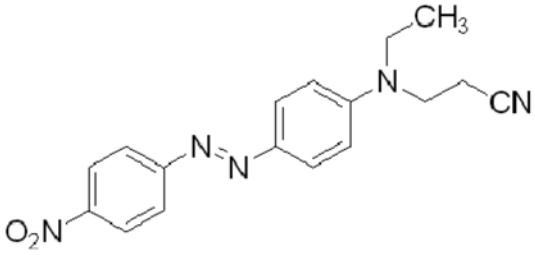

Fig. 2. Chemical structure of DO25.

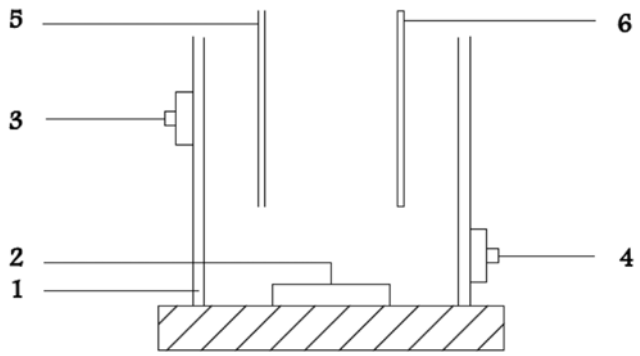

Fig. 3. Schematic diagram of sonoreactor.

1. Cooling water jacket
2. Transducer
3. Cooling water inlet
4. Cooling water outlet
5. Sampling tube
6. Thermometer

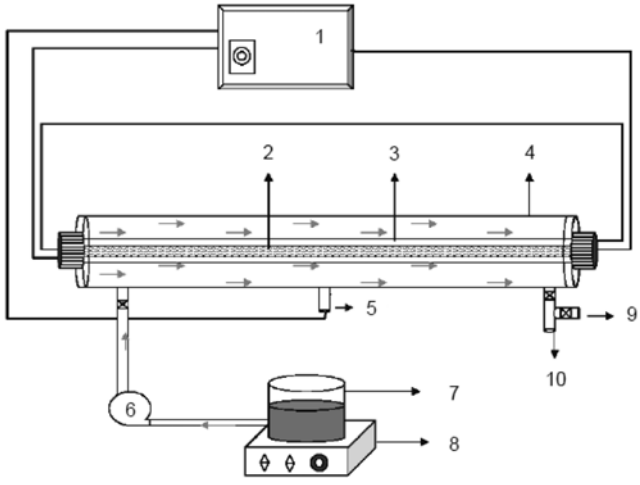

Fig. 4. Schematic diagram of photoreactor.

1. Transformator
2. Low pressure Hg UV lamp
3. Quartz jacket
4. Stainless steel jacket
5. Photocell
6. Pump
7. Dye vessel
8. Shaker
9. Sampling tube
10. Outlet tube

30 °C. The concentration of dyes in solution samples was determined at the maximum absorption wavelength with 10 mm glass cell using a double beam spectrophotometer (PJ Instrument-T 80, England). The maximum wavelengths λ_{max} (nm) for the dyes studied were determined as 597 and 425 nm for the RB5 and DO25, respectively. COD was measured according to standard methods [21].

Acute toxicity of dyes and the toxic effects of their degradation products after degradation processes were studied with *Daphnia magna* test according to standard methods [21]. Primary daphnia was caught from their living site, and then one of them was cultured alone, after infants of primary daphnia were used for culture in large amounts. Based on our earlier study [20], groundwater was suitable for bioassay tests using *D. magna* and the general characteristics were as follows: pH 7.8, total hardness 137 mg L^{-1} as $CaCO_3$, total alkanity 300 mg L^{-1} as $CaCO_3$, electrical conductivity 1,215 μS cm^{-1}, calcium 38 mg L^{-1}, magnesium 9 mg L^{-1}, chloride 60 mg L^{-1}, sulfate 153 mg L^{-1} and nitrate 37 mg L^{-1}. *D. magna* was maintained in a 10 L glass vessel containing culture medium in a temperature-controlled condition of 22±2 °C and a 12/12 light-dark cycle. For running the experiment, 10 infants (age<24 h) were exposed to the test volume of 100 ml in a 250 ml glass beaker. The initial concentration of dyes was 50 mg L^{-1}. Experimental concentrations tested were 100, 50, 25, 12.5, 6.25 and 3.125% of each effluent diluted with dilution water. After the setting periods of 24 and 48 hours, LC_{50} values were calculated for toxicity tests by use of the special computer program [PROBIT] [22]. Finally, for a certain comparison, the toxicity values were converted to toxic units (TU). The TU of an effluent or mixture is equal to 100% divided by the LC_{50} of that effluent or mixture [23]. All experiments were run in triplicate to ensure reproducibility.

RESULTS AND DISCUSSION

The advanced oxidation of the RB5 and DO25 at different initial concentration in the range 10-50 mg L^{-1} was investigated. Initial results demonstrated that neither US nor US plus H_2O_2 was able to appreciably decolorize RB5 and DO25 (50 mg l^{-1}). Figs. 5-8 show the degradation of both dyes as function of time. As can be seen, sonochemical decoloration proceeded very slowly leading to less

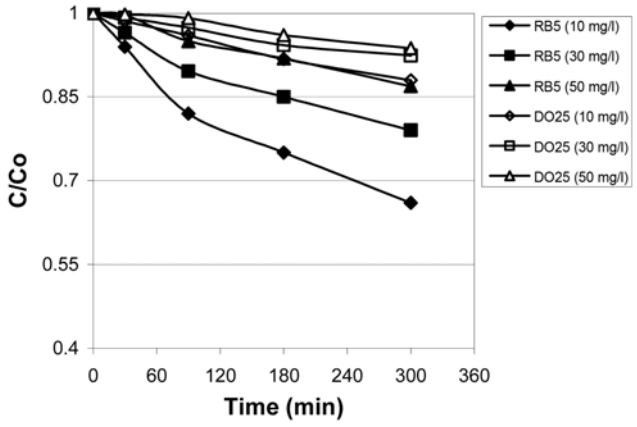

Fig. 5. Effect of initial RB5 and DO25 concentrations on sonodegradation efficiency at different times.

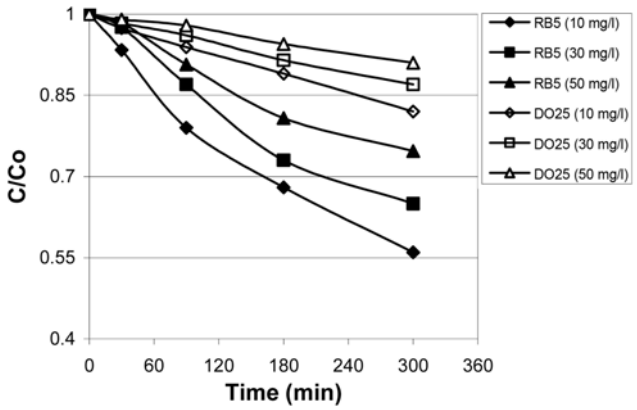

Fig. 6. Effect of initial RB5 and DO25 concentrations on US/H_2O_2 process efficiency at different times.

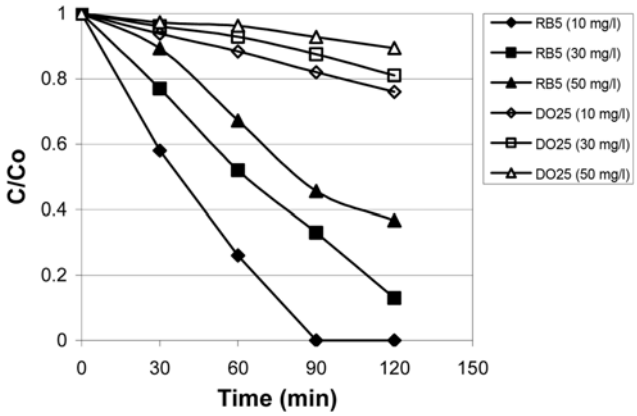

Fig. 7. Effect of initial RB5 and DO25 concentrations on photodegradation efficiency at different times.

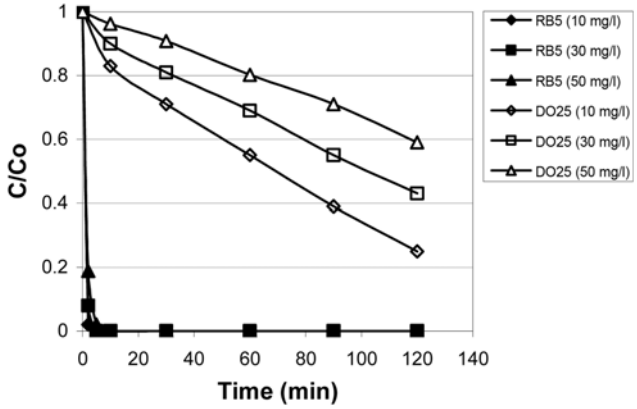

Fig. 8. Effect of initial RB5 and DO25 concentrations on UV/H_2O_2 process efficiency at different times.

than 13.1% of RB5 removal and 6.3% of DO25 removal after 300 min. It can also be observed from results that UV had its potential to degrade RB5. More than 60% decoloration was achieved after about 120 min at 50 mg l^{-1} of RB5. DO25 showed more resistance than the RB5, and the maximum decolorization efficiency obtained for DO25 was around 10.6% after 120 min of irradiation in UV

processes. Disperse dyes comprise organic nonionic compounds that are generally characterized by their low solubility in water. They can be structurally classified as mainly azo, anthraquinone, nitrophenylamino and triphenylmethane chromophoric systems [24]. According to previous studies, the direct photodegradation of disperse dyes is difficult mainly due to their low aqueous solubility [24].

The poor effects of US alone on the decolorization efficiency may be attributed to the fact that low ultrasound frequencies hinder the development of hydroxyl radicals [25]. Hence, for RB5, a nonvolatile and highly soluble compound, reactions inside or in the vicinity of the bubble (where fast thermal decomposition and increased concentrations of radicals exist) are unlikely to occur to an appreciable extent and, therefore, its degradation will be driven by hydroxyl radical-mediated secondary activity in the liquid bulk. Thus US process generally demands a high contact time for significant degradation efficiency [26]. Instead, UV light had high potential to produce the highly reactive hydroxyl radical. This would explain discrepancies in reactivity of RB5 between sonochemical and photolytic reactions since the latter involve the participation of a more diverse range of reactive species (i.e., radicals and electrons) than the former [20, 27]. However, considering the operating conditions in this study, UV light performance does not seem to be efficient for DO25 decoloration. This is mainly due to the fact that DO25 has low aqueous solubility. On the other hand, most commercially used dyes are typically designed to be light resistant, which makes degradation under UV light particularly difficult. Therefore, the combination of UV with H_2O_2 was necessary for the production of hydroxyl radicals to initiate the decolorization of the concerned dyes at a reasonable time scale even for the higher dye concentrations. These results are in good agreement with other findings in literature, such as Aleboyeh et al. [28] who showed that a combination of UV plus H_2O_2 in comparison with UV alone increases removal rates of Acid Orange 8 and Methyl Orange, 172 and 137 times, respectively. In this view, the UV radiation is combined with a powerful oxidant, H_2O_2; the degradation efficiency of the dye is significantly enhanced due to hydroxyl radical production caused by the photolysis of H_2O_2, as reported by other researchers [29]. This condition led to a rapid decolorization of RB5 and more than 40% decolorization of DO25 after about 120 min. However, in the absence of H_2O_2, only 10.6% decolorization of DO25 was obtained. Since H_2O_2 concentrations are important factors which influence the decolorization rate of both dyes by UV photolysis in the presence of hydrogen peroxide, a series of experiments were conducted in order to optimize initial H_2O_2 concentration. For this purpose hydrogen peroxide concentrations were selected between 10-70 mmol L^{-1}. Fig. 9 shows the effect of different H_2O_2 concentrations on degradation efficiency of RB5 and DO25. It can be seen the photodegradation efficiency increases with an increase in the amount of H_2O_2 concentration, up to the optimum value and then decreases when the H_2O_2 concentration is increased. This trend can be explained by the fact that H_2O_2 itself acts as an effective hydroxyl radical 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 [30]. It can be concluded that a H_2O_2 dose higher than 20 and 50 mM for RB5 and DO25, respectively, corresponds to an unprofitable consumption of H_2O_2. The DO25 was shown to be more difficult to be decolorized than RB5 in these oxidation processes. Thus, it can be seen that the chemical structures of dyes affect the decolorization efficiency. According to literature, the direct photodegradation of disperse dyes is difficult mainly due to their low aqueous solubility [24]. In addition to the physicochemical properties of the dye, degradation efficiency of dyes by direct photolysis is dependent upon reactivity and photosensitivity of the dye. Most commercially used dyes are usually designed to be light resistant, which makes degradation under UV light in the absence of an additional agent particularly difficult [31]. The retention time for 6% removal of DO 25 in US, US/H_2O_2, UV and UV/H_2O_2 processes was 300, 190, 75 and 20 min, respectively. It has also been pointed out that the decolorization rates gradually decreased with increas-

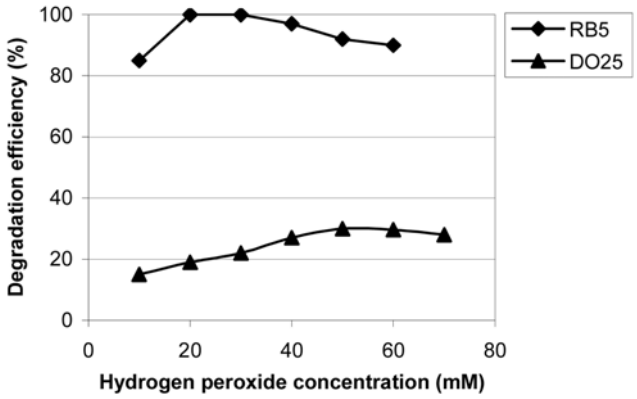

Fig. 9. Effect of different H_2O_2 concentrations on degradation efficiency of RB5 and DO25 (Irradiation times=30 min, dye concentration=10 mg L^{-1}).

Table 1. Pseudo first order rate constants for the different dyes degradation processes at different initial dyes concentration

Type of process		RB5 concentration (mg^{-1})			DO 25 concentration (mg^{-1})		
		10	30	50	10	30	50
US	Rate constant (min^{-1})	0.0066	0.0037	0.0023	0.0019	0.0012	0.0009
	Correlation coefficient	0.98	0.98	0.94	0.94	0.95	0.91
US/H_2O_2	Rate constant (min^{-1})	0.0089	0.0066	0.0045	0.0029	0.0021	0.0014
	Correlation coefficient	0.97	0.93	0.92	0.94	0.94	0.94
UV	Rate constant (min^{-1})	0.0153	0.0067	0.0037	0.0045	0.0025	0.0017
	Correlation coefficient	0.99	0.99	0.96	0.99	0.96	0.97
UV/H_2O_2	Rate constant (min^{-1})	0.1304	0.0842	0.0442	0.0162	0.0099	0.0059
	Correlation coefficient	1	1	0.98	0.95	0.96	0.93

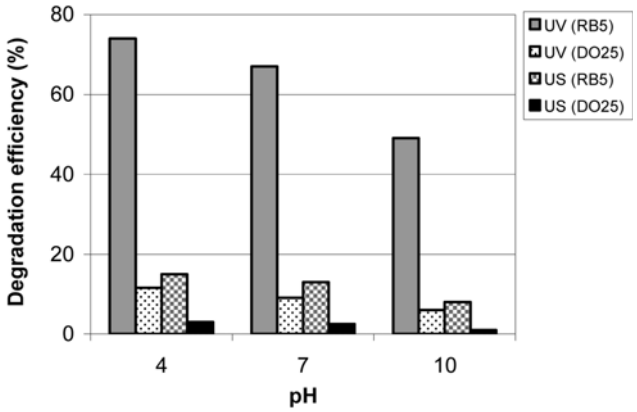

Fig. 10. Effect of pH on degradation efficiency of RB5 and DO25 (Irradiation times=60 min, dye concentration=10 mg L^{-1}).

ing initial dye concentrations (Table 1). Nevertheless, the efficiency of the process in terms of the amount of dye decolorized generally increased at higher initial concentrations. The presumed reason is that when the initial concentration of dye is increased, the competition between the dye intermediates and parent dye for hydroxyl radical became intense owing to the non-selective reactivity of hydroxyl radical. Additionally, in the US process with increasing initial dye concentration the cavities approached saturation [32]. The two factors contributed to a decreasing rate constant for the decolorization of both dyes with an increase in initial concentration.

As demonstrated in Table 1, the decolorization of a dye solution by oxidation processes exhibited pseudo-first-order reaction kinetics. The pseudo-first-order rate constants (k) of decolorization obtained from the slope of $-\ln(C/C_0)$ vs. t (time) plots where C_0 and C are dye concentration at time zero and at time t, respectively. The rate of dye decolorization was dependent on the dye's initial concentration (C_0) and k decreased with increasing C_0. These results are in good agreement with other findings in the literature [10,33].

In further experiments, dye decolorations were carried out at various pH (4-10) during oxidation processes (Fig. 10). It is notable that decoloration depends strongly on the solution pH and is substantially reinforced at acidic conditions, while hindered at alkaline conditions. For instance, the extent of RB5 decoloration (10 mg L^{-1}) after 60 min photolysis at pH values of 4, 7 and 10 was 74%, 67% and 49%, respectively. This acceleration is probably associated with the effect of protonation of negatively charged -SO_3 groups in acidic medium and, obviously, the hydrophobic character of the resulting molecule enhances its reactivity under oxidation processes [34]. Moreover, under acidic pH, hydroxyl radical is the predominant reactive oxidant and under alkaline pH, hydroperoxyl (HO_2) radicals do not have as high oxidizing power as hydroxyl radical. Hydroperoxyl radical (HO_2), also known as the perhydroxyl radical, is produced from the reaction of H_2O_2 with hydroxyl radicals. Also under extreme alkaline conditions, H_2O_2 scavenging effects become more significant [34]. Therefore, hydrogen peroxide scavenges the photogenerated oxidizing species and reacts with hydroxyl radicals, thus decreasing the amount of hydroxyl radicals which will react with the dye.

The dye toxicity was evaluated for dye solutions before and after the decolorization processes with *D. magna*. Results showed that

Table 2. Acute toxicity toward *Daphnia magna* after 48 h of exposure

Type of solution test	RB 5		DO 25	
	LC_{50} (% v/v)	Toxicity unit (TU)	LC_{50} (% v/v)	Toxicity unit (TU)
Parent dye	2.96	33. 8	2.24	44.6
US effluent	4.21	23.7	2.85	35.0
US/H_2O_2 effluent	1.35	74.0	1.35	74.0
UV effluent	13.25	7.5	5.58	17.9
UV/H_2O_2 effluent	1.35	74.0	1.35	74.0

both dyes were toxic to *D. magna* and resulted in quite low LC_{50} values. This means that the concentration values of the dyes used are considered toxic to the aquatic environment and that color removal is required. As can be seen in Table 2 the acute toxicity tests with *D. magna* showed lesser toxicity than the parent form of both dyes after UV and US processes. However, the UV process was more effective than the US process in reducing dye toxicity. The toxicity level of dye solutions after US plus H_2O_2 and UV plus H_2O_2 processes was even higher than the toxicity level found for the dye solution without any color removal treatment, indicating that even with the removal of 100% of the dye RB5 from the aqueous solution, an expressive mortality of the *D. magna* occurred. One possible reason for this increase in toxicity, after treatment, could also be due to the presence of residual H_2O_2 in the effluents. Comparison of UV and UV plus H_2O_2 processes efficiency showed that both oxidation processes led to complete dye elimination (especially RB5) and there was no difference between UV and UV/H_2O_2 in terms of dye degradation results. However, in this special case it can be simply observed from Table 2 that there is a difference between UV and UV/H_2O_2 in terms of bioassay results. In other words, toxicity unit (TU) decreased from 33.8% to 7.5% after photolysis while it increased from 33.8% to 74% after photolysis plus H_2O_2.

This point must also be noted, that although the intermediate compounds have not been determined, they certainly have been produced and the existence of the toxicity in the samples after UV process with complete dye destruction should be related to the intermediates of the dyes. On the other hand, because the UV/H_2O_2 process is more efficient than the UV process, the intermediates' destruction is therefore more under the former process. Even if there is no difference between UV and UV/H_2O_2 processes in terms of intermediates' destruction results, the results of bioassay should be the same in both processes. But, it is clear that toxicity unit increased after photolysis plus H_2O_2. In other words, we can draw a conclusion that another agent might have killed all bioandicators, which is presumably due to the presence of the residual of H_2O_2 in samples. This hypothesis was confirmed by measuring the amount of hydrogen peroxide and 2 to 4 mg L^{-1} of it was observed in the end of the destruction process. This is not far from reality, because in order to optimize initial H_2O_2 concentration, concentration interval was 10 mg L^{-1} and therefore, the obtained optimum concentration of hydrogen peroxide may not be accurate. This means that there should be an optimum H_2O_2 concentration both for maximizing the dye degradation and for minimizing the toxicity increase. Accordingly, this is another point worthy of note for application of H_2O_2.

CONCLUSIONS

In this experimental study, decolorization of RB5 and DO25 was investigated by using several advanced oxidation processes: US, US plus H_2O_2, UV and UV plus H_2O_2. The influence of operating parameters, pH value, initial concentration of dye and initial H_2O_2 concentration was investigated and estimated on the basis of UV/VIS. Optimal operating conditions for each process were established. The conclusions drawn from this study can be summarized as follows:

• The decolorization efficiency proceeded very slowly when US, US plus H_2O_2 and UV processes were used.

• The experimental results demonstrated that the UV plus H_2O_2 process could be a suitable pre-treatment method for complete decolorization for RB5, once the optimum operating conditions are established.

• The decolorization efficiency was found to increase with increasing H_2O_2 concentration; however, the marginal benefit became decreasing with further increasing of H_2O_2 due to the scavenging effect of excess H_2O_2.

• DO25 was more resistant to all decolorization processes with respect to RB5.

• The extent of decoloration depends on the operating conditions employed such as the type and concentration of H_2O_2, initial dye concentration and solution pH.

• Low frequency (42 kHz) ultrasound irradiation of both dye solutions is far less efficient than UV and UV plus H_2O_2 in degrading both dyes, presumably because sonochemical activity is driven by secondary (and less efficient) radical reactions in the liquid bulk.

• The rate of color decay followed pseudo-first order kinetics with respect to the UV-visible absorption of the test dye during reaction.

• Both dyes examined were toxic to *D. magna* and resulted in quite low LC_{50} values.

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NOMENCLATURE

k : first order constant [min^{-1}]

LC_{50} : the statistically determined concentration that causes 50% mortality in a given exposure period [mg $^{L-1}$]

TU : toxicity unit [%]

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