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Degradation of Reactive Red 194 and Reactive Yellow 145 azo dyes by O_3 and H_2O_2/UV-C processes

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ABSTRACT

Reactive Red 194 (RR194), Reactive Yellow 145 (RY145) azo dyes and synthetic textile dye-bath effluent were treated with O_3 and H_2O_2/UV-C processes. The operating parameters such as dye concentration, hydrogen peroxide concentration and pH values were evaluated to find the optimum conditions for the H_2O_2/UV-C processes. It was observed that while H_2O_2/UV-C process was more pH dependent in decolorization and dearomatization reactions, ozonation was less selective and more effective in both decolorization and dearomatization reactions. Results indicated that the decolorization and dearomatization rate of each dye are well defined by pseudo-first order reaction kinetics. In general, decolorization reactions were faster than dearomatization reactions in both systems, though ozonation had faster reaction rates in both decolorization and dearomatization compared to the corresponding reaction rates taking place during the application of the H_2O_2/UV-C process. According to decolorization efficiency it can be inferred that effect of OH radical scavengers (e.g. CO_3^{2-}, Cl^-) present in the synthetic dye-bath as well as radical formation promoter (e.g. OH^-) was probably hidden due to complexity of the synthetic dye-bath matrix.

1. Introduction

The azo dyes, which are widely used in the textile industry, can be hazardous to the environment due to their reactivity, toxicity and recalcitrance. Conventional methods including coagulation, activated carbon adsorption and membrane filtration have been used for decolorizing the wastewater. However, these methods cannot completely destruct pollutants and need further disposal as well as increasing the treatment cost well.

In recent years, alternative to conventional methods "advanced oxidation processes" (AOPs; O_3/UV, O_3/H_2O_2, H_2O_2/UV, etc.), based on the generation of very reactive species such as hydroxyl radicals, which oxidize a broad range of organic pollutants in aqueous media quickly and non-selectively, are being developed [1–3]. Ozonation and other advanced oxidation techniques (UV/H_2O_2, TiO_2/UV, photo-Fenton and photo-catalytic oxidation) have also been used for the treatment of textile wastewaters some of which contained azo dyes [4–11].

Ozone reacts with organic compounds dissolved in water through either direct ozone attack or indirect free radical attack. The predominance of the oxidation reactions by molecular ozone at a lower pH has already been established, while some critical pH level (pH > 7) hydroxyl radicals might become the predominant oxidizing species [12].

Direct reaction of ozone with dye molecule occurs as follows [13]:

$$O_3 + \text{dye} \rightarrow \text{dye}_{\text{oxid}} \quad (\text{oxidationproductofdye})$$

Indirect reaction occurs with the reactions:

$$O_3 + H_2O \xrightarrow{OH^-} OH^{\bullet} + O_2$$

$$OH^{\bullet} + \text{dye} \rightarrow \text{dye}'_{\text{oxid}}$$

The H_2O_2/UV oxidation process is one of the AOP, and it has potentially practical importance [5,6]. The main reactions of this process are generating OH radicals and oxidizing of dye molecule occurred as follows:

$$H_2O_2 + UV \rightarrow 2OH^{\bullet}$$

$$OH^{\bullet} + \text{dye} \rightarrow H_2O + \text{dye}^{\bullet} \rightarrow \text{further} \quad \text{oxidation}$$

Several dyes have been successfully degraded by this technique [5,14,15]. Comparison of ozonation and H_2O_2/UV oxidation process was studied by various researchers. Pre-ozonation coupled with UV/H_2O_2 process was studied by Shu and Chang [8] for the decoloratization and mineralization of cotton dyeing effluent and synthesized C.I. black 22 wastewater. They found that UV/H_2O_2

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process took longer retention time than ozonation for color removal of dye-bath effluent. Reversely, removal efficiency of the total organic carbon (TOC) was obtained 33% and 90% for ozonation and UV/H_2O_2 process for 160 min reaction time, respectively. Therefore, pre-ozonation coupled with UV/H_2O_2 process was employed to enhance the reduction of both color and TOC in dye-bath effluent at the same time. O_3, UV/O_3 and UV/H_2O_2 processes were studied by Shu and Chang [9] for decolorization of six azo dyes (C.I. Acid Orange 10, C.I. Acid Red 14, C.I. Acid Red 18, C.I. Acid Yellow 17, C.I. Direct Yellow 4, and C.I. Acid Black 1). They reported that it was more difficult to decolorize the dyes with dis-azo links than mono-azo dyes. However, when they compared energy required for processes, they found that UV/H_2O_2 system required about 5–11 and 265–520 times more energy than that of UV/O_3 process and ozonation process, respectively. Alaton et al. [10] compared O_3, H_2O_2/UV-C and TiO_2/UV-A processes for reactive dye-bath effluent. They reported that the ozonation reaction exhibited instantaneous decolorization kinetics and reasonable TOC reduction rates.

Several reports have been published in the last decade on using catalytic and UV-enhanced ozonation for RR194 and RY145 azo dye removal. The mineralization of RY145 aqueous solution using UV-enhanced ozonation was investigated by Song et al. [16]. The results indicated that ozonation combined with UV radiation was more efficient than ozonation alone or UV irradiation for the removal of TOC. Gül et al. [11] investigated catalytic role of granular activated carbon (GAC) on the degradation and mineralization of RR194 and RY145 in aqueous solution by treatment with ozone. The results indicated that ozonation was strong enough to decolorize azo dyes and almost all COD disappeared but efficient mineralization had not been achieved. The extent of TOC removal was about 25% when no GAC had been used and this value doubled in the presence of GAC.

The RR194 and RY145 azo dyes are very common in cotton dyeing. The dyes have both sulphatoethylsulphone (SES) group and monochlorotriazine (MCT) group. Therefore, they were chosen as representative azo dyes to comparatively study by O_3 and H_2O_2/UV-C processes. The objective of this study was to compare the performances of O_3 and H_2O_2/UV-C processes on degradation of RR194 and RY145 azo dyes in aqueous solutions. Optimum pH, dye and hydrogen peroxide concentrations were investigated to find the best optimum condition for decolorization and dearomatization of RR194 and RY145 azo dyes. Optimum reaction pH and oxidant dose were determined by measuring the absorbance values of treated aqueous solutions at 522 and 419 nm (max absorption wavelengths), the absorbance of aromatics at 280 nm and TOC removal for RR194 and RY145, respectively. In addition to that, synthetic dye-bath effluents with dye mixture were prepared to simulate conventional batch dyeing effluents and investigate the effects of this matrix on ozonation performance.

2. Materials and methods

2.1. Materials

The hetero bi-functional reactive azo dyes (RR194 and RY145) were obtained from Eksoy Tekstil (Adana) and used without further purification. The chemical structures and characteristics of dyes were given in our previous study [11].

The solutions of RR194 and RY145 were prepared by dissolving the dyes (20–100 mg/L) in deionized water. Following oxidative treatments, the aqueous solutions were filtered through 0.2 μm Millipore syringe filter prior to analytic investigations (TOC and UV/vis absorbance).

Table 1
Chemical composition of the synthetic dye-bath effluent.

Component	Concentration (g/l)	Function
Reactive Red 194 (RR194)	1	–
Reactive Yellow 145 (RY145)	1	–
Na_2CO_3 (Soda)	20	Adjustment of the starting alkaline pH
NaCl	6	Promotes exhaustion of the dye onto cotton
Antisil ACC	0.5	Removes unwanted metal ions in the dye-bath water

2.2. Preparation of the synthetic dye-bath effluent

Synthetic dye-bath effluent was prepared as a mixture based on a recipe most widely used in the reactive cotton dyeing process. The recipe was obtained from a local textile manufacturing plant (Eksoy Tekstil, 2009). The composition of the simulated effluent and functions of the additives in the mixture are presented in Table 1 as 10-fold diluted amounts. Three types of dye simulated solutions were ozonated. One of them contained unhydrolysed dye mixture at pH 11. Other dye mixture solution was prepared by adding soda-ash alone. The last solution was prepared by adding all the components in the recipe. The purpose of this experiment is to investigate the hydroxyl radical scavenging effects of carbonate and chloride ions and also other additives on the performance of ozonation processes (O_3/OH^- treatment, $O_3/CO_3{}^{2-}$ scavenger, O_3/full recipe).

Samples periodically withdrawn from the ozone reactor were filtered through 0.2 μm Millipore syringe filter prior to analytic investigations (TOC and UV/vis absorbance). The A_{436} value in the visible spectra region was chosen as color parameter according to the European Industrial Standard EN ISO 7887:1994-12 [17], whereas the absorption at 280 nm was indicative for organic species having an aromatic structure.

2.3. Advanced oxidation treatments

Ozonation reaction was carried out by passing ozone gas through the aqueous dye solution (1000 ml) with an O_3 dose of 28 mg/min in a 1 l, stirred semi-batch lab scaled glass reactor. A magnetic stirrer was used to mix the reactor contents. Ozone was produced from pure oxygen in an ozone generator (Hermann) with a gas flow rate of 0.8 L/min. Two wash bottles full of 2% KI solution were connected in series to quench the unreacted ozone gas leaving the reactor in the exit of the reactor. Ozone concentrations in the feed and reactor effluent were determined using the iodometric procedure for each ozonation sequence (IOA, 1987). Most of the test runs lasted for 30 min. Samples (ca. 5 ml) were withdrawn at regular times for analysis. All ozonation experiments were conducted at room temperature.

H_2O_2/UV-C oxidation of dyes was conducted in a 1 l capacity photo-reactor. The reactor was equipped with a 20 W low pressure mercury vapour UV-C lamp (Pen-Ray). UV-C lamp emitted 98% of its total irradiation at 254 nm. The reactor was loaded with 1000 ml of the dye aqueous solution consisting of different initial dye concentrations (20–100 mg/L), initial pHs (3, 7 and 11) and variable initial H_2O_2 dosages range of 5–80 mM (170–2720 mg/L). An excess of hydrogen peroxide with respect to the dye was added (400 mol:1 mol) so that concentration of H_2O_2 could be considered as a constant during the whole experiment. As in the case of the ozonation experiments all H_2O_2/UV-C reactions were performed at ambient temperature and no lamp cooling was provided.

Table 2
Percent color, UV_{280} and TOC removal efficiencies for ozonation of azo dyes at varying pHs ($C_{0(\text{dye})}$ = 100 mg/L, ozone dose = 28 mg/min, treatment time = 30 min).

Initial pH	% decrease in		% decrease in		TOC removal (%)	
	A_{522}(RR194)[a]	A_{419}(RY145)[b]	A_{280}(RR194)[c]	A_{280}(RY145)[d]	RR194	RY145
3.0	96.77	99.48	88.08	93.18	11.03	28.64
7.0	96.83	99.02	91.24	91.86	30.53	29.02
11.0	98.89	99.54	92.00	93.46	35.49	43.80

[a] % decrease in decolorization of RR194 aqueous solution based on light absorption at 522 nm.
[b] % decrease in decolorization of RY145 aqueous solution based on light absorption at 419 nm.
[c] % decrease in light absorption of RR194 aqueous solution at 280 nm indicating aromatic ring degradation.
[d] % decrease in light absorption of RY145 aqueous solution at 280 nm indicating aromatic ring degradation.

2.4. Analytical procedure

The absorbance of the original and treated samples was determined by using a Shimadzu UV-2101 PC double beam spectrophotometer. The decolorization of RR194 and RY145 solutions was monitored via absorbance measurements at 522 nm (A_{522}) and 419 nm (A_{419}), respectively. Dearomatization was monitored by measuring the absorbance at 280 nm (A_{280}). The concentration of the residual dye in solution was calculated using a calibration curve at the characteristic wavelength.

TOC values were performed on a Tekmar-Dohrman Apollo 9000 TOC analyzer. In a typical application, 10 ml aliquot withdrawn from the reaction medium at certain intervals were ignited at 700 °C on platinum-based catalyst. Carbon dioxide formed was swept by pure oxygen as the carrier gas through a nondispersive infrared (NDIR) detector.

The concentration changes of chloride, sulphate, nitrite, nitrate and ammonium ions were monitored by ion chromatography (IC, Shimadzu LC-10AD*vp*). The IC was equipped with a CDD-6A conductivity detector, a Shodex I-524 anion and Shimpack IC-CI cation exchange columns. The samples were filtered through a 0.20 μm membrane NC 20 filter (Schleicher & Schuell) and introduced directly into the HPLC injector port.

2.4.1. Kinetic evaluation

The kinetic study was supported on the decolorization and dearomatization of the azo dye. Assuming pseudo-first order reaction kinetics with respect to the dye concentration, decolorization and dearomatization rates were described as k_d and k_{UV280}, respectively:

$$-\ln\left(\frac{C}{C_0}\right) = kt$$

where C and C_0 are the dye concentration at time t and 0, respectively and k is the pseudo-first order rate constant (1/time) for decolorization (k_d) and for dearomatization (k_{UV280}).

3. Results and discussion

3.1. O_3 treatment

To determine the optimum pH value, pH of the dye solutions was adjusted to 3, 7 and 11 and each subjected to ozonation for 30 min. Fig. 1 displays the time dependent changes in color and UV_{280} absorption abatement kinetics at varying pH values for each dye. Decolorization (degradation of diazo linkage between aromatic structures and thus, decreasing of π conjugation) took place more effectively in basic solution in comparison to neutral and acidic media for both RR194 and RY145 (Fig. 1b and d and Table 2). Also, one can deduce that decolorization was faster in RY145 solutions in comparison to the corresponding rates of reactions taking place in RR194 solutions. Like decolorization, dearomatization, i.e. degradation of aromatic rings (decrease in UV_{280} absorbance) also took place more effectively in alkali solution in comparison to neu-

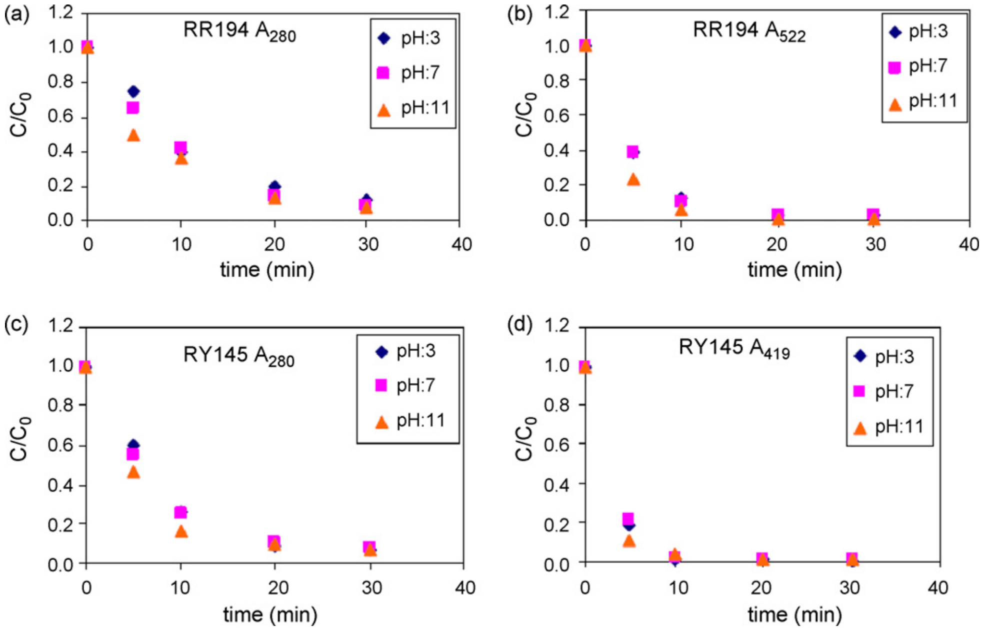

Fig. 1. Variations in normalized concentrations (C/C_0) of RR194 and RY145 vs treatment time. A_{280} for RR194 (a), A_{522} for RR194 (b), A_{280} for RY145 (c), A_{419} for RY145 (d) for ozonation at varying pHs. Applied ozone dose = 28 mg/min.

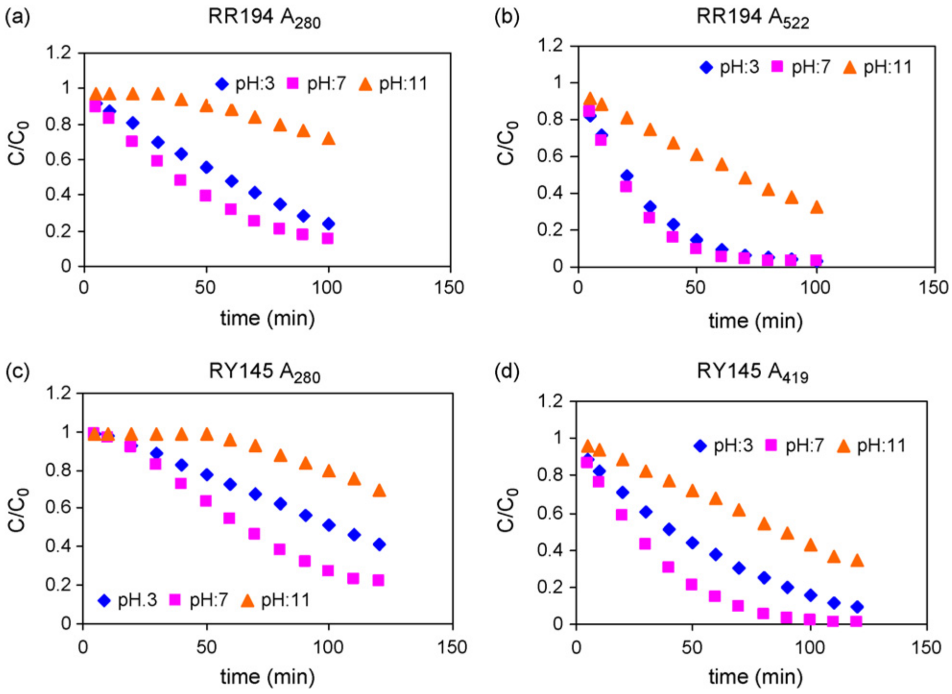

Fig. 2. Variations in normalized concentrations (C/C_0) of RR194 and RY145 vs treatment time. A_{280} for RR194 (a), A_{522} for RR194 (b), A_{280} for RY145 (c), A_{419} for RY145 (d) for H_2O_2/UV-C at varying pHs. $C_{0(\text{dye})}$ = 100 mg/L, $C_{0(H_2O_2)} = 40$ mM.

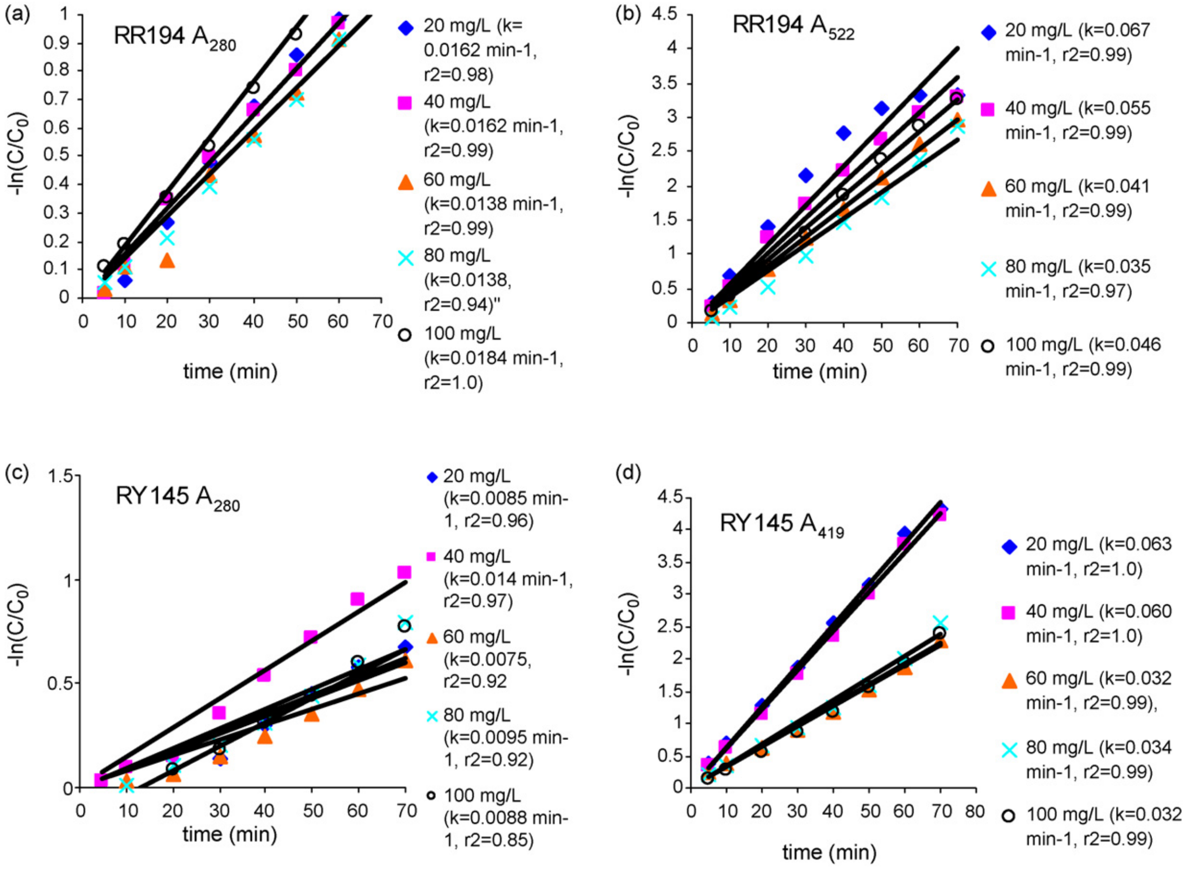

Fig. 3. UV$_{280}$ and color abatement kinetics; A_{280} for RR194 (a), A_{522} for RR194 (b), A_{280} for RY145 (c), A_{419} for RY145 (d) for H_2O_2/UV-C at varying dye concentrations. pH 7.0, $C_{0(H_2O_2)} = 40$ mM.

Table 3
Percent color, UV_{280} and TOC removal efficiencies for UV/H_2O_2 oxidation of azo dyes at varying pHs ($C_{0(\mathrm{dye})} = 100$ mg/L, $C_{0(H_2O_2)} = 40$ mM, treatment time = 120 min).

Initial pH	% decrease in		% decrease in		TOC removal (%)	
	A_{522}(RR194)	A_{419}(RY145)	A_{280}(RR194)	A_{280}(RY145)	RR194	RY145
3.0	96.17	90.98	71.14	58.87	20.43	14.34
7.0	96.72	99.22	85.58	77.70	25.70	26.10
11.0	62.26	65.88	23.64	30.09	8.73	10.14

tral and acidic media for both RR194 and RY145. One can also note that some aromatic structures (~10%) still persist while the decolorization of both dye solutions were almost complete at the end of 30 min ozone treatment.

Decolorization and reduction in UV_{280} absorbance percentages and TOC reduction efficiencies obtained after 30 min ozonation are summarized in Table 2.

As can be seen in Table 2, a high degree of decolorization and dearomatization could be achieved by employing O_3 under the stated conditions but TOC removal efficiencies were not as high as the previous ones. More than 50% of organic carbon was still in the aqueous solution. This result indicated that either a higher rate of ozone application or a longer duration of treatment should be necessary to achieve complete mineralization. Since the hydroxyl radical created by O_3 in alkali medium attacks the chromophore of dyes, it causes the breakage of molecular bonds. Therefore, the color is resolved continuously and this turns to be faster than TOC.

3.2. UV/H_2O_2

3.2.1. Effect of pH

To explore the effect of pH and initial dye concentration on the H_2O_2/UV-C treatment efficiency, the experiments were carried out at pH 3, 7 and 11 for 120 min treatment time, using 100 mg/L dye solutions and 40 mM H_2O_2.

As can be seen in Fig. 2, complete color removal was achieved following 80 min oxidation, whereas dearomatization (decrease in UV_{280} absorbance) was not completed even after 100 min of treatment at pH 7 for each dye.

Table 3 presents the percent decolorization and dearomatization values as well as overall percent TOC removal efficiencies obtained for UV/H_2O_2 oxidation at varying pH values.

Table 3 shows that the performance of the treatment in terms of TOC removal was rather low and about 75% of organic TOC was still in solution. It can be deduced that satisfactory decolorization and dearomatization could be achieved with 2 h treatment given processing conditions. However, increase of hydrogen peroxide concentration in the reaction medium relative to the dye concentration during the whole treatment; i.e. addition of hydrogen peroxide with an optimum rate to the reaction medium will be necessary to achieve an efficient TOC removal by employing H_2O_2/UV-C oxidation. Because the reaction mechanism for H_2O_2/UV-C oxidation of dyes is rather complex, it is more widely accepted that UV destroys H_2O_2 into highly reactive hydroxyl radicals, which are the key species in the process [18]. The reaction rates of the two dyes were rather slow in alkaline media. This considerable decrease in rate at pH 11 can be attributed to the decomposition of hydrogen peroxide in alkaline medium leading to dioxygen and water, rather than producing hydroxyl radicals under UV irradiation [5].

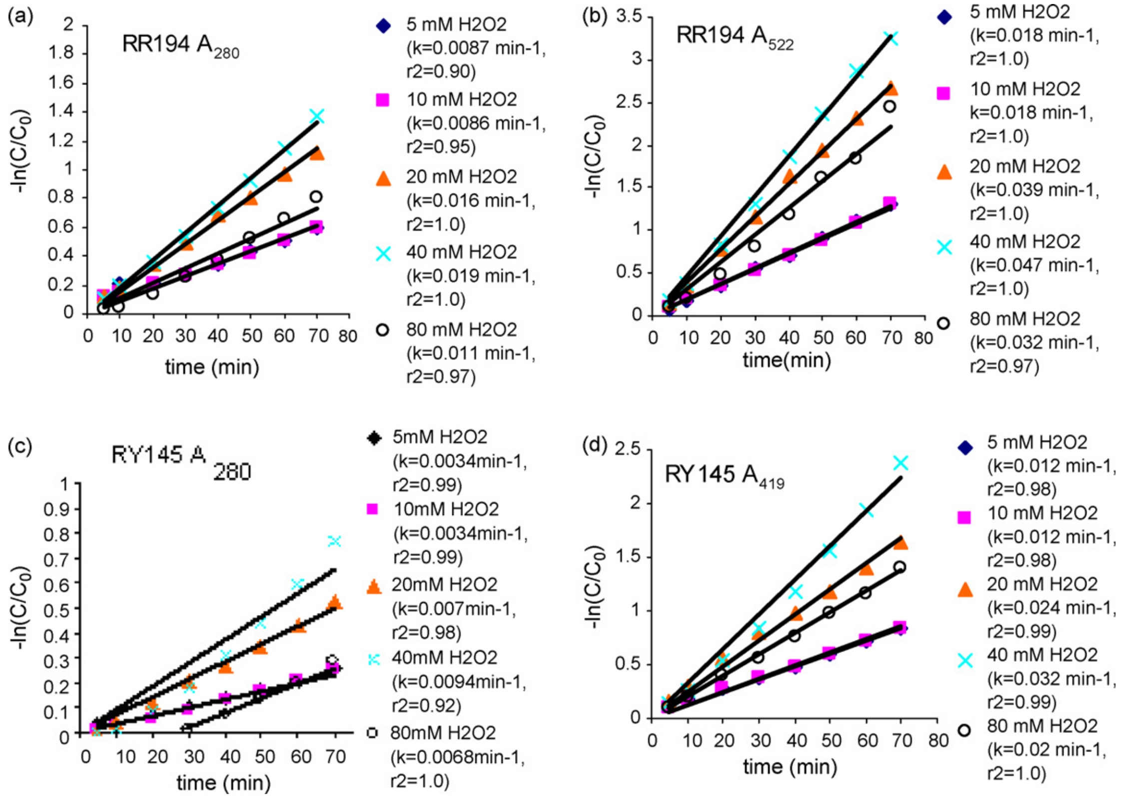

Fig. 4. UV_{280} and color abatement kinetics; A_{280} for RR194 (a), A_{522} for RR194 (b), A_{280} for RY145 (c), A_{419} for RY145 (d) for H_2O_2/UV-C at varying H_2O_2 concentrations. pH 7.0, $C_{0(\mathrm{dye})} = 100$ mg/L.

Table 4
Formation and evolution of chloride, nitrite, nitrate and sulphate ions during O_3 and H_2O_2/UV-C processes.

AOP/treatment time	Cl^- (mg/L)		NO_2^- (mg/L)		NO_3^- (mg/L)		SO_4^{2-} (mg/L)	
	RR194	RY145	RR194	RY145	RR194	RY145	RR194	RY145
O_3/0 (min)	10.35	8.35	0	0	1.41	0	8.46	18.33
O_3/5 (min)	9.81	7.98	0.65	1.60	3.90	4.57	17.27	33.13
O_3/30 (min)	9.44	7.98	0.98	1.43	11.53	12.32	29.96	39.48
H_2O_2/UV/0 (min)	8.71	7.88	0	0	0	0	4.58	10.22
H_2O_2/UV/30 (min)	8.90	7.44	0	0	1.51	1.57	8.46	18.33
H_2O_2/UV/60 (min)	7.22	7.62	0	0	1.83	1.95	13.74	23.61

The decolorization experiments of each dye were carried out with 20, 40, 60, 80 and 100 mg/L initial concentrations at pH 7. One can notice in Fig. 3 that the more dilute the initial concentration, the faster is the decolorization as expected. By increasing the initial concentration from 40 to 80 mg/L, the apparent k_d-values for decolorization decreased from 0.060 to 0.034 and 0.055 to 0.035 min^{-1} for RY145 and RR194, respectively. On the other hand, the fastest UV_{280} absorption abatement in RR194 was obtained with 100 mg/L initial dye concentration ($k_{UV280} = 0.0184\,min^{-1}$), while for RY145 the fastest dearomatization reactions took place in solution with 40 mg/L initial dye concentration ($k_{UV280} = 0.0141\,min^{-1}$).

3.2.2. Effect of initial H_2O_2 concentration

The effect of initial H_2O_2 concentration on the decolorization of each dye was examined by applying 5, 10, 20, 40, 60 and 80 mM H_2O_2 concentrations at pH 3.0. The removal rates considerably increased by increasing the initial H_2O_2 concentration and reached a maximum value at 40 mM H_2O_2 concentration for color and UV_{280} absorption abatement kinetics (Fig. 4). When H_2O_2 concentration was increased from 40 to 80 mM, the color abatement rate decreased about 1.6-fold for RY145. The apparent k_d was found as 0.032 and 0.020 min^{-1} at 40 and 80 mM H_2O_2 concentration for RY145, respectively. These values were correspondingly 0.047 and 0.032 min^{-1} for RR194. UV_{280} absorption abatement rates were also reached highest value when the initial concentration of H_2O_2 was 40 mM for both dyes (k_d found as 0.0094 and 0.019 min^{-1} for RY145 and RR194, respectively). It can be concluded that further increase in the initial H_2O_2 dose above 40 mM caused an inhibition on the H_2O_2/UV-C process performance because H_2O_2 itself acts as an $OH^•$ scavenger [5,14]:

$$H_2O_2 + OH^• \rightarrow HO_2^• + H_2O$$

Thus, it is very important to optimize the applied H_2O_2 dose to maximize the treatment performance of the AOP.

3.3. Fate of chlorine, sulphur and nitrogen atoms in the dye molecule

To further understand whether inorganic ions are released or not, in the O_3 and H_2O_2/UV-C processes of RY145 and RR194 azo dyes, ion chromatography was utilized to determine the levels of inorganic anions and ammonium cation during reactions. The results in Table 3 show that no significant chloride ion change was detected during the reaction. However, nitrite, nitrate and sulphate levels increased when the reaction time was increased. Ammonium ion was not produced during both of the processes. Since the protonation of amine groups are needed for the formation of ammonium ions, one can conclude that formation of acidic groups should be more favourable in both of the processes. While the chlorine atoms in the dye molecules existed in the stabile triazine form, nitrogen and sulphur atoms were partially mineralized and were released in the forms of inorganic ions. It was apparent that sulphonyl group linked to the naphthalene ring was more easily mineralized than chlorine linked to the triazine ring when the concentrations of mineralization products were compared. Therefore, sulphate ion concentrations were higher than chloride and nitrate ions. Table 4 indicates that Cl^- and SO_4^{2-} ions were released by ambient air oxidation. The slight decrease in chloride concentration following initial O_3 and H_2O_2/UV-C processes may be due to further oxidation of Cl^- to OCl^- and Cl_2 species [11]. Both dyes contain three sources of nitrogen including an azo group, a triazine ring and a nitrogen atom linking naphthalene and benzene ring for RY145 and RR194, respectively. Table 3 shows that the formation of nitrite ions took place only by ozonation in both of the dyes. It might be due to primary attacks of O_3 on the double bonds of azo group, resulting in the formation of unstable by-product nitrite ions. The mineralization of naphthalene and triazine rings by hydroxyl radicals formed by ozonation at alkali medium and by H_2O_2/UV-C process was converted C–N bond to nitrates. Therefore, the concentrations of nitrates were found ten times than that of nitrites.

3.4. Comparative evaluation of the AOPs

The performances of the selected AOPs in terms of decolorization, dearomatization and mineralization of azo dyes were evaluated by measuring the light absorptions at 522 and 419 nm, UV absorption at 280 nm and TOC values for decolorization, dearomatization and mineralization, respectively. According to Table 5, the first order decolorization and dearomatization reaction rates were fastest at pH 11 for both dyes. The H_2O_2/UV-C process was less efficient than ozonation for all types of degradation reactions; i.e. decolorization, dearomatization and mineralization. It has longer decolorization, dearomatization and mineralization durations in comparison to ozonation. As it is apparent to Table 5, k_d-values were higher by factors of 3:15, 5:30 RY145, respectively and k_{UV280} values were higher by factors of 5:43, 13:165 for RR194 and RY145, respectively.

3.5. Ozonation of simulated dye-bath effluent

In an attempt to relate our present study, it was decided to formulate a simulated spent dye-bath and test its response for ozonation. This experiment was carried out for the only ozonation

Table 5
First order rate constants of decolorization and dearomatization reactions during treatments of dye solutions with O_3 and H_2O_2 at varying pHs.

AOPs	k_d (min^{-1})		k_{UV280} (min^{-1})	
	RR194	RY145	RR194	RY145
O_3				
pH 3.0	0.1554	0.1807	0.0759	0.1089
pH 7.0	0.1491	0.1711	0.0857	0.1123
pH 11.0	0.1877	0.2448	0.0900	0.1157
H_2O_2/UV-C				
pH 3.0	0.0382	0.0185	0.0122	0.0051
pH 7.0	0.0466	0.0371	0.0191	0.0088
pH 11.0	0.0101	0.0081	0.0021	0.0007

Table 6
The characterization of RR194 and RY145 dyes, dyes + soda and full recipe in ozonation process during 30 min treatment.

Dye-bath components	TOC%	A_{280}%	A_{436}%
RR194 + RY145 (dyes)	33	87.81	99.11
Dyes + soda	25	73.65	99.11
Full recipe	21	73.31	97.52

process because it was found more effective than UV/H_2O_2 process through studied individual experiments for the degradation of reactive dyes.

In order to examine the influence of adding chemicals (salts, soda and chelating agent) on ozonation, the experiment was carried out in the absence and present of these chemicals. The results were presented in Table 6.

The extent of mineralization was negatively influenced from the soda and complex background matrix, which are the synthetic dye-bath effluent components. Carbonate and chloride are well hydroxyl radical scavengers. Therefore, both mineralization and dearomatization were affected from their presence. However, color removal efficiency was not significantly affected from dye-bath components.

4. Conclusions

The following conclusions can be drawn from this experimental work.

Comparing the investigated O_3 and H_2O_2/UV-C processes, the fastest color ($k_d = 0.25\,\text{min}^{-1}$ and $k_d = 0.19\,\text{min}^{-1}$ for RY145 and RR194, respectively), UV_{280} ($k_{UV280} = 0.12\,\text{min}^{-1}$ and $k_d = 0.19\,\text{min}^{-1}$ for RY145 and RR194, respectively) and highest overall TOC removal (43.8% and 35.5% for RY145 and RR194, respectively) were obtained by ozonation at pH 11. When compared to ozonation of RY145 and RR194, the differences of decolorization, dearomatization and TOC values were due to stability of naphthalene ring of RR194 to mineralization. The general concepts of ozone (namely, the enhancement of oxidation efficiency and kinetics at pH 11) as well as AOP chemistry (generation hydroxyl radicals at alkali media) were valid for the almost complete decolorization and partial mineralization of azo dyes.

H_2O_2/UV-C treatment proceed relatively slowly even at neutral pH where the highest decolorization ($k_d = 0.047$ and $0.032\,\text{min}^{-1}$ for RR194 and RY145, respectively), dearomatization ($k_{UV280} = 0.0191$ and $0.0088\,\text{min}^{-1}$ for RR194 and RY145, respectively), and the highest TOC reduction rate (25.7% and 26.1% for RR194 and RY145, respectively) were achieved. The optimum H_2O_2 concentration in the UV-C light assisted H_2O_2 process for decolorization and dearomatization of azo dyes was observed as 40 mM for both dyes. Because of its inherent advantages (i.e. infinite solubility in water, no sludge formation, minimal capital investment and easy operation procedure), the H_2O_2/UV-C process remained the most applied AOP for the treatment of wastewater.

The O_3/OH^- was sufficient to remove 33% TOC, 99.11% color and 87.81% aromaticity of the dye mixtures at alkaline pH (11) in only 30 min. A fraction of more than 67% of the dye mixture remained in the end of the experiment. It becomes evident the reaction trend is as follows: azo reactive dyes are degraded to refractory daughter products. In view of these experimental results it can be concluded that ozonation might be more feasible on the enhancement of chemical oxidation of reactive dyes than UV/H_2O_2 process.

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