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Reactive dye effluent treatment with peroxide-assisted ozonation: Effects of persulfate, peracetic acid and percarbonate

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Abstract−Simulated reactive dyebath effluent (pH≈11.0-11.5) bearing the commercially important textile azo dye Reactive Red 21 (100 mg/L) can be successfully decolorized via ozone (feed rate=72 mg/min) and peroxide (=0.75-6.00 mM)/ozone treatment processes. Persulfate (PS), peracetic acid (PAA) and percarbonate (PC) were selected as alternative oxidants to the more conventional hydrogen peroxide. Color (peak absorbance) and total organic carbon (TOC) removals increased with increasing PS concentration, but decreased when PC was introduced due to free radical scavenging effects of carbonate alkalinity. PAA improved color and TOC removal rates, but thereby also contributed to the TOC content of the dyebath effluent. PAA-assisted ozonation showed the highest performance in terms of color removal at an optimum PAA concentration (=1.5 mM). According to the gas phase-and-dissolved ozone measurements, addition of the peroxides PS-PAA enhanced ozone decomposition and increased ozone absorption rates whereas PC addition stabilized aqueous, molecular ozone. The originally non-toxic reactive dyebath effluent (≈10% relative inhibition) did not exhibit serious acute toxicity towards *Vibrio fischeri* photobacterium throughout ozonation and ozone/PS treatment, whereas a slight increase was observed for ozone/PAA-ozone/PC that decreased with applied ozone dose. The 7th-day-biochemical-oxygen-demand (BOD_7; <10 mg/L) decreased with ozone dose speaking for less biodegradable oxidation products.

Keywords: Reactive Dyebath Effluent, Peroxide-assisted Ozonation, Color, Total Organic Carbon, Acute Toxicity, Biodegradability

INTRODUCTION

The majority of industries, including chemical, pharmaceutical, cosmetics, textile, printing and tannery sectors, use dyes and/or related products in massive amounts. Regarding the annual production of commercially important textile dyestuffs with approximately 1.28×10^6 tons produced annually, reactive dyes constitute around 45% of the overall market share [1,2]. Reactive dyes are mainly applied to cellulose, regenerated cellulose and cotton fibers via alkaline fixation, forming covalent bonds with the fibers. However, an appreciable fraction (up to 30%) remains unfixed in the exhausted reactive dyebath [2,3]. Since unfixed dyes are hydrolyzed via alkali treatment, they cannot be re-used and are ultimately discharged into the textile wastewater treatment plant [1-3]. At the same time, a high percentage of textile dyes are of the azo (-N=N-) type, that is a classification according to the chromophore group in their structure [4,5]. In fact, most colors are produced via azo dyes (namely yellow, red, brown, orange and black shades); hence azo dyes are the most prevalent and largest in the textile market [1,3]. From the environmental point of view, commercial reactive dyes are originally non-toxic, and the major ecological problem of dyes is their persistent (bioresistant) nature due their synthetic origin and complex polyaromatic structure [3-5]. Several advanced treatment methods have been investigated so far for color removal from dyehouse effluent, including reverse osmosis, coagulation/flocculation, activated carbon adsorption, adsorption with natural biosorbents and zeolites, ion exchange as well as many other physical-chemical processes and unit operations [6-13]; however, with rather limited success in terms of performance, design and economic feasibility. Moreover, most of these methods only transfer the pollutants from one phase to another, creating an additional solid waste management problem. However, ozonation has proven to be a more successful and technically feasible treatment process for colored wastewater [14-21]. Ozone, which has a high reduction potential of 2.08 V under acidic pH conditions, selectively attacks dye chromophores and hence is particularly effective in terms of color removal [5,8,22-27]. However, there are some disadvantages of ozonation, including its absorption (utilization) efficiency, and thus high dosing requirements and operating (electricity) costs. Therefore, extensive research has been devoted to the combination of ozone with other oxidants, catalysts, photocatalysts and/or UV-C light to enhance its oxidation capacity [26-33]. So-called "advanced oxidation processes" (AOPs) have received considerable attention in the last three decades due to their high performance in the destruction of toxic and/or refractory industrial pollutants found in water/wastewater [28,30,34-38]. The most powerful reactive oxygen species (ROS) that is known as the hydroxyl radical ($HO^\bullet$) attacks a majority of organic molecules at diffusion-limited rates [37-39]. AOPs combine power-

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ful oxidants such as ozone and hydrogen peroxide (HP), heterogeneous (photo)catalysts/semiconductors, transition metal ions and metal oxides, short-wavelength (high energy), electromagnetic radiation like UV-C light, cavitation/sonolysis/ultrasound (US) or electron beams to form these ROS [34-39]. The so-called "green" (ecologically safer) oxidants such as persulfate (PS), peracetic acid (PAA), and percarbonate (PC) have been relatively less explored compared with hydrogen peroxide (HP) and can also produce free radicals such as sulfate ($SO_4^{\bullet-}$; E^0=2.5-3.1 eV) and carbonate ($CO_3^{\bullet}$; E^0=1.6-1.8 eV) via thermal, electromagnetic, catalytic, photocatalytic, chemical and photochemical activation methods [40-48]. They are known to be more stable, long-lived and selective than $HO^{\bullet}$, which can be an advantage in color and organic carbon removal [49-51]. Several PS-activation methods for water/wastewater treatment have already been investigated so far as promising alternatives to HP-activation methods [50-52]. The peroxide PAA is also a strong oxidant and reacts to acetic acid and HP in water. PAA is used as a broad-spectrum antimicrobial agent in water treatment applications as well as by food, medical and textile industries [53]. PAA is known to have a redox potential (=1.96 eV) between HP (=1.78 eV) and PS (=2.10 eV). As HP or PS, PAA can be activated to form $HO^{\bullet}$ besides acetyloxy radicals ($CH_3C(=O)O^{\bullet}$) that quickly decompose into methyl- ($CH_3^{\bullet}$) and peroxy ($CH_3O_2^{\bullet}$) radicals continuing the chain reaction. Percarbonate (PC) on the other hand could also serve as the oxidant for alternative peroxide-activation methods. PC dissociates in water into HP and carbonate ions; the formed HP reacts with bicarbonate and peroxymonocarbonate (HCO_4^-) to form $HO^{\bullet}$ and carbonate radicals ($CO_3^{\bullet}$) upon activation. In this way, redox potentials increase to initiate free radical chain reactions for pollutant removals.

At the same time, the above-mentioned peroxides (HP, PS, PAA and PC) are called "green" since these peroxides and their degradation products are known to be less toxic and hence more environmentally friendly than active chlorine chemicals [53-55]. So far, the peroxides PS, PC and PAA have not been studied in combination with ozone for color removal from reactive dyebath effluent.

Considering the above-mentioned issues, the present study investigated the treatability of a simulated reactive dyebath effluent bearing a commercially important, reactive diazo dye (Reactive Red 21; RR21) selected as the model industrial pollutant and two dye assisting chemicals commonly used in the reactive dyeing process (namely, the electrolyte sodium chloride and the alkali fixation agent soda ash) with ozone and PS, PAA and PC-assisted ozonation (peroxide/ozone) processes at varying peroxide concentrations. The ultimate purpose of this study was to convert the reactive dye molecules into more biodegradable and/or less toxic degradation/oxidation intermediates and/or end-products. The simulated reactive dyebath effluent was subjected to high-rate ozonation (72 mg/min) in the absence and presence of the peroxides PS, PAA and PC at varying concentrations (0.75-6.00 mM). The treatment performance was followed as color (peak absorbance of RR21) and total organic carbon (TOC); for ozonation and ozone/peroxide experiments under varying reaction conditions. Changes in ozone chemistry and hence the reaction pathway were verified following gas-phase ozone absorption rates ($O_{3,A}$; in %) and dissolved molecular ozone concentrations ($C_{O3,L}$; in mg/L) at the end and throughout ozone and ozone/peroxide treatments, respectively. Besides, changes in acute toxicity and biodegradability of the reactive dyehouse effluent before and after ozone and ozone/peroxide treatments were measured by employing an acute toxicity test with the marine photobacteria *Vibrio fischeri* and 7th-day biochemical oxygen demand (BOD_7) tests with acclimated sewage sludge, respectively.

MATERIALS AND METHODS

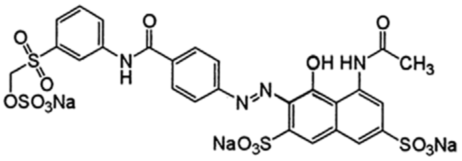
1. Materials

All chemicals were of at least analytical grade and purchased from Sigma-Aldrich, Turkey. The reactive dye RR21 was a gift from Eksoy Chemicals (Adana, Turkey). Some physicochemical properties of RR21 are illustrated in Table 1.

2. Preparation of the Hydrolyzed Reactive Dyebath Effluent

A reactive dyebath effluent containing RR21 dye was prepared and used in the ozonation and ozone/peroxide experiments. The selection of this reactive dye type/reactive dye recipe was based on previous related publications and preliminary treatability studies considering the high performance of ozonation in the degradation of reactive dyes and color removal from reactive dyehouse effluent [1,2,56,57]. The "exhausted" reactive dyebath was simulated by dissolving RR21 in hot (80-85 °C), distilled/de-ionized water and adding the dye assisting chemicals NaCl and Na_2CO_3 into this hot solution. Thereafter, the pH of this solution was directly increased to ≈11.4-11.5 with concentrated NaOH solution to ensure com-

Table 1. Physicochemical properties of the RR21 dye

Characteristic	Value
Molecular formula	$C_{26}H_{19}N_4Na_3O_{15}S_4$
Molecular weight (g/mol)	824.68
Molecular structure	
Peak absorbance (nm) at pH≥11.0*	520
Appearance	Red powder

*pH suitable for complete reactive dye hydrolysis

Table 2. Chemical composition/ingredients of the simulated reactive dyebath used in the experimental study

Reactive dyebath ingredients	Concentrations (g/L)
RR21 (hydrolyzed reactive dye)	1.0
Na_2CO_3 (alkali reagent)	15.0
NaCl (electrolyte)	50.0

plete hydrolysis of the dye in a couple of minutes instead of hours [1,2]. The alkali reagents (soda-ash, caustic soda) used the during reactive dyeing process release the vinyl sulphone group of the reactive dye and initiate covalent bond formation between the dye's reactive group and the cellulosate anions [2]. The exact composition of the simulated (spent, exhausted) reactive dyebath is presented in Table 2.

The reactive dyehouse effluent was prepared for the ozonation and ozone/peroxide experiments after 10-fold dilution of the simulated, exhausted reactive dyebath (composition shown in Table 2), resulting in a 100 mg/L hydrolyzed, alkaline RR21 solution to mimic the composition of typical dyehouse effluent after reactive dyeing, rinsing and prior to finishing (pH=10.8-11.2; average pH= 11.0) processes [1,2,56].

3. The Ozonation Set-up

A 1,000-mL capacity borosilicate glass bubble column reactor was used for the ozonation experiments with reactive dyehouse effluent samples. The ozone contactor was continuously sparged with an ozone+oxygen mixture at a constant flow rate of 2.0 L/min from the reactor bottom through a sintered glass plate diffusor at semi-batch mode with respect to ozone feed rate. Ozone was produced from dry, pure oxygen (Plusmed, Turkey) using an ozone generator (SE-5 Model SABO Electronic, Turkey) having a maximum ozone production capacity of 3.8 g/h and continuously fed to the reactor at a rate of 72 mg/min. Ozone feed rate (inlet) and off-gas (outlet) concentrations were measured by iodometric titration [58], while the mass transfer coefficient of the ozonation set-up was determined as $k_{La}=0.02\ s^{-1}$ using the indigo colorimetric method [58]. Ozonation experiments in the presence of PS, PAA and PC were carried out through the addition of potassium persulfate ($K_2S_2O_8$), sodium percarbonate ($Na_2CO_3 \cdot 1.5H_2O_2$) and peracetic acid ($C_2H_4O_3$), respectively, to 1,000 mL RR21 dyehouse effluent and stirred vigorously for at least 10 min to ensure complete dissolution of the peroxides prior to the ozonation experiments. Samples were taken at regular time intervals up to 40 min (=2,880 mg ozone) during ozonation and PS, PC- and PAA-assisted ozonation experiments for pH, color (peak absorbance), TOC, gas phase/bulk ozone concentrations, BOD_7 and acute toxicity measurements.

4. Analytical and Instrumental Procedures

The color of the samples was measured at the peak absorbance values of the hydrolyzed RR21 dyes (520 nm) using a Jenway 6300 model spectrophotometer (Cole-Parmer, UK). A Shimadzu VPCN model carbon analyzer (Japan) equipped with an autosampler was used for the TOC analysis of selected samples. A Thermo Orion 720A model pH-meter (Waltham, USA) was used for all pH adjustment and measurements. The BOD_7 in the original and ozonated/perozonated samples was measured according to Standard Methods [58] using acclimated heterotrophic biomass (sewage sludge) taken from the textile industry wastewater plant (practicing activated sludge treatment) of a local dyehouse. The acute toxicity was measured with a commercial test kit following the ISO 11348-3 test protocol [59] and calculated as the percent relative photoluminescence inhibition towards the gram negative, rod-shaped marine photobacterium *V. fisch*eri (also called *Aliivibrio fischeri*). Prior to bioassays, 1.5 mM thiosulfate solution was added to all treated samples to remove any residual, unreacted peroxide. Then the pH of all samples was adjusted to 7.2-7.4 with 0.5 M HCl solution. Two parallel sets per sample were prepared and the luminescence intensities were recorded in all test tubes including controls, after t=15 and 30 min; however, t=30 min was reported in this study.

5. Statistical Evaluation

Statistical analyses were undertaken for TOC instrumental results as well as calculation of the color removal rate coefficients (k_d values; in min^{-1}) using MS Office Excel. Duplicates were used to carry out bioassays with the photobacterium *V. fischeri*. Bioassays were tested for statistical significance using the software provided by the Aboatox and MicroBioTests. The significance level in all calculations was set at $p \leq 0.05$.

For the calculation of k_d values, the following first-order kinetic equation was applied for peak absorbance A (cm^{-1}) of the dye and ozonation time t (in min);

$$\ln(A_o/A)=k_d \times t \tag{1}$$

RESULTS AND DISCUSSION

1. Color Removal

It has been demonstrated that ozonation of organic compounds such as industrial dyes at alkaline pH decomposes molecular ozone to free radicals and hence involves the participation of mainly hydroxyl ($HO^{\bullet}$), superoxide ($O_2^{\bullet-}$) and hydroperoxyl ($HO_2^{\bullet}$) radicals as well as the more selective bicarbonate ($HCO_3^{\bullet}$) and carbonate ($CO_3^{\bullet-}$) radicals that may become dominant depending on the pH and alkalinity of the reaction solution [34,40,60]. In the present study, the effect of the peroxides PS, PAA and PC was examined and compared with ozonation alone at the natural pH of the diluted reactive dyebath effluent (pH≈11.0 after 10-fold dilution of the original reactive dyebath given in Table 2) in the concentration range of 0.75-6.00 mM peroxide. This concentration range was selected to achieve a specific stoichiometry (molar concentration ratio) between the peroxide and molecular ozone in the reaction solution [61-64]. For the peroxide concentration effect runs, 0.75, 1.50, 3.00 and 6.00 mM peroxides were tested during ozonation experiments and compared with ozonation only (0.00 mM peroxide). During all ozonation experiments, color abatements followed pseudo-first-order kinetics with respect to peak absorbance and color removal occurred within 2-4 min corresponding to an ozone dose of 144-288 mg. Fig. 1 presents the first-order color removal rate coefficients - k_d values (in min^{-1}) - calculated for varying peroxide concentrations (0-6 mM) (a) and also presented as the "mM Peroxide : mM Ozone" ratio (b) during ozone/peroxide treatments of the RR21 dyebath effluent. In this section results obtained with ozone/peroxide treatments were compared with ozonation alone (with no-0.00 mM peroxide; or mere ozonation). Note that during all ozo-

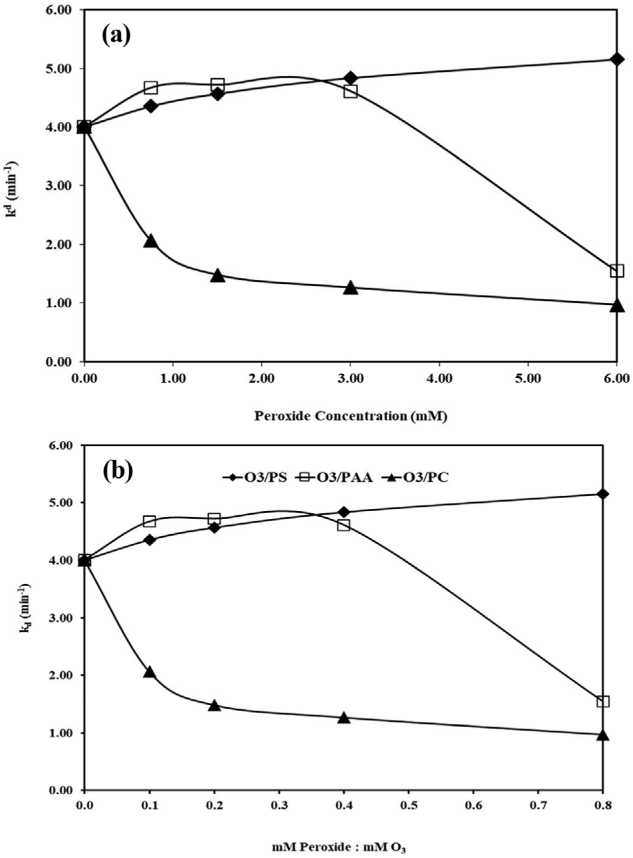


Fig. 1. Effect of peroxide (PS, PAA and PC) concentrations (a) and the peroxide: ozone molar ratios (b) on k_d values (in min^{-1}) for RR21 dyebath effluent treatment with ozone and ozone/peroxide. Experimental conditions: Ozone feed rate=72 mg/min; ozonation time=5 min; inital RR21 concentration=100 mg/L; initial absorbance=1.5 cm^{-1}; initial pH=11.0; peroxide concentration range=0.75-6.00 mM.

nation and ozone/peroxide experiments, the pH values did not decrease to less than pH=10.6 (after O_3/PAA) due to the high alkalinity of the reaction solution.

Considering PS: from Fig. 1(a), (b) it can be seen that the addition of PS appreciably increased k_d values for RR21 effluent treatment from 4.0 min^{-1} calculated for ozonation only to 5 min^{-1} in the presence of the highest studied PS concentration (6.00 mM). The higher the PS concentration, the faster was color removal and the k_d values increased with increasing the PS concentrations from 0.75 to 6.00 mM. The highest studied concentration of 6.00 mM PS reduced the ozone dose required for complete color removal from 144 mg to 108 mg, which would have a serious positive effect on operating costs, particularly the electric energy requirements to produce ozone gas, that is, 10-15 kWh/kg ozone [65]. Considering ozone chemistry, it is known that PS addition results in the formation of different ROS and initiation of free-radical chain reactions due to enhanced ozone decomposition having similar effects of alkaline decomposition of molecular ozone [61,62]. That is, the positive effect of PS addition on color removal can be explained via reactions given in Eqs. (2) through (6), where ozone decomposition into $HO_2^{\bullet}$, $HO^{\bullet}$ and $SO_4^{\bullet-}$ occurs under alkaline pH values in the presence of PS [62-64,66];

$$O_3+HO^- \rightarrow HO_2^- + O_2 \qquad k=7.0\times10^1\ M^{-1}\ s^{-1} \qquad (2)$$

$$O_3+HO_2^- \rightarrow HO_2^{\bullet}+O_3^{\bullet-} \qquad k=2.2\times10^6\ M^{-1}\ s^{-1} \qquad (3)$$

$$O_3^{\bullet-}+H_2O^- \rightarrow HO^{\bullet}+O_2+HO^- \qquad k=3.0\times10^1\ M^{-1}\ s^{-1} \qquad (4)$$

$$HO^{\bullet}+S_2O_8^{2-} \rightarrow SO_4^{\bullet-}+HSO_4^-+½\ O_2 \qquad (5)$$

$$SO_4^{\bullet-}+H_2O^- \rightarrow SO_4^{2-}+HO^{\bullet}+H^+ \qquad (6)$$

In addition to the above reactions, a pH (≥9) could directly activate PS through hydrolysis reactions [67] into $SO_4^{\bullet-}$ and $O_2^{\bullet-}$, as shown in Eqs. (7) to (9);

$$S_2O_8^{2-}+H_2O \rightarrow SO_5^{2-}+SO_4^{2-}+2H^+ \qquad (7)$$

$$SO_5^{2-}+H_2O \rightarrow HO_2^-+SO_4^{2-}+H^+ \qquad (8)$$

$$S_2O_8^{2-}+HO_2^- \rightarrow SO_4^{\bullet-}+SO_4^{2-}+H^++O_2^{\bullet-} \qquad (9)$$

Our findings for color removal with O_3/PS were consistent with previous research, which reported that O_3/PS treatment is more effective than mere ozonation and that PS addition enhanced oxidation with ozone [61-63]. PS addition also improved the treatment of stabilized (old) landfill leachate for hard-to-degrade color and TOC removals in the presence of PS [62].

The peroxide PAA, a relatively recently explored oxidant, is a mixture of H_2O, H_2O_2, and CH_3CO_2H [41,68-72] with a rather high reduction potential (1.76 V). It is produced as shown in reaction Eq. (10);

$$CH_3CO_2H+H_2O_2 \rightarrow CH_3CO_3H+H_2O \qquad (10)$$

Some favorable features of PAA include ease of operation, low pH dependence and lack of mammal toxicity [41,43]. Unfortunately, due to its inherent selectivity, PAA cannot efficiently degrade most organic contaminants without activation [69-72]. The activated PAA, however, can generate $HO^{\bullet}$ and a number of organic radicals ($R^{\bullet}$), such as the acetoxyl and acetylperoxy radicals ($CH_3CO_2^{\bullet}$ and $CH_3CO_3^{\bullet}$, respectively) that can effectively degrade organic pollutant molecules in water/wastewater [41,68,71,72]. Therefore, activation of PAA appeared to be a promising alternative to the more well-known HP. In the present study, the effect of increasing PAA concentrations (0.75-6.00 mM) on the k_d values calculated for color (peak absorbance) removal rates is also depicted in Fig. 1. As obvious from Fig. 1, a slightly different kinetic pattern was evident for O_3/PAA treatment of RR21 effluent compared with O_3/PS; at the concentrations of 0.75, 1.50 and 3.00 mM PAA, the color removal rate constant was enhanced to 4.6-4.7 min^{-1}. However, the addition of 6.00 mM PAA had a negative effect on color removal rates and the k_d value abruptly decreased to 1.5 min^{-1} indicating that an "overdose" exceeding the optimun concentration of PAA resulted in a free radical scavenging (competitive inhibitory) effect in terms of color removal rates [71,72]. From the experimental results shown in Fig. 1 it is evident that the concentration of PAA needs to be carefully optimized because unneccessarily high PAA concentrations in the reaction solution would result in an additional TOC (total TOC, RR21+TOC, PAA=113 mg/L at t=0 min) that would also competitively react with the in-situ formed $HO^{\bullet}$. Moreover, the additional oxygen-centered, more selective $CH_3C(O)O^{\bullet}$ and

$CH_3C(O)OO^\bullet$ radicals generated through PAA-activation could also play a role in the oxidation of RR21 and its degradation products [42]; however, at slower rates than $HO^\bullet$. The above-mentioned findings revealed that PAA, once activated by ozone-mediated free radical chain reactions initiates the formation of active oxidants, but a PAA overdosing could result in competitive, free radical scavenging reactions, thereby also contributing to the surplus organic carbon concentration (measured as TOC) in the reaction solution [52].

PC is another type of peroxide that has frequently been used as a household bleaching and cleaning agent [73]. Additionally, PC provides an inherent transport safety as compared with HP and can be used throughout a broad pH range as PS and PAA. Numerous studies have demonstrated that PC can degrade organic contaminants more efficiently than HP [73-75]. However, PC has rarely been combined with ozone, which is interesting from the practical point of view, particularly for dyehouse effluent treatment. Once added into water, PC decomposes to CO_3^{2-} and H_2O_2 (=H_2O+O_2), the former which is already in the reaction solution as a dye assisting (alkali fixation) reagent (soda-ash) in the reaction solution (RR21 reactive dyehouse effluent) [73,74];

$$2Na_2CO_3{\cdot}3H_2O_2 \rightarrow 4Na^+ + 2CO_3^{2-} + 3H_2O_2 \tag{11}$$

In this study, PC was initially added to the RR21 effluent at a concentration range of 0.75-6.00 mM. Fig. 1 presents PC/O_3 treatment results together with the other ozone combinations in terms of color removal rates (a). Fig. 1 also shows changes in k_d values with respect to the peroxide PC : O_3 molar ratio during PC/O_3 treatment of RR21 effluent (b). In the presence of PC and at alkaline pH, O_3 decomposes into $HO^\bullet$, CO_2, H_2O and CO^{2-}, the latter known as a strong $HO^\bullet$ scavenger. The presence of PC thus encourages the conversion of $HO^\bullet$ to $CO_3^{\bullet-}$. Its reduction potential (=1.57 V) is much lower than that of $HO^\bullet$ (=2.76 V) [28,61]. Further, the presence of bicarbonate/carbonate alkalinity in water/wastewater increases its alkalinity and may raise its pH [60,76]. $HO^\bullet$ scavenging reactions with both of the alkalinity species are given below (Eqs. (12), (13));

$$HCO_3^- + HO^\bullet \rightarrow HCO_3^\bullet + HO^- \qquad k=4.6\times10^7\ M^{-1}\ s^{-1} \tag{12}$$

$$CO_3^{2-} + HO^\bullet \rightarrow CO_3^{\bullet-} + HO^- \qquad k=3.2\times10^8\ M^{-1}\ s^{-1} \tag{13}$$

Fig. 1 also illustrates the effect of increasing PC concentration and that adding PC decreased the color removal rate constants from 4.00 min^{-1} (no PC addition) in the absence of PC down to 1.00 min^{-1} with 6.00 mM PC. For example, the time needed for complete color removal decreased from 2.0 min (144 mg O_3) to 5.0 min (360 mg O_3) upon increasing the PC concentration from 0.00 mM to 6.00 mM, respectively. These findings suggest that the overdosed PC scavenged $HO^\bullet$, as given in Eq. (12) and particularly (13), that is the dominant alkalinity form at pH=11. In another related study, the removal of dichlorvos was significantly inhibited when the reaction pH was increased from the natural (original) solution pH (≈7) to pH=10 during PC-assisted ozonation (pH=10; dichlorvos=4 mg/L; PC=30 mg/L; O_3 dose=4.21 mg/L).

From the above experimental findings it is evident that in particular PS but also PAA for the concentrations 0.75-1.50-3.00 mM accelerated color removal rates during ozonation of RR21 reactive dyehouse effluent, while PC addition resulted in a reduction of color removal rates under otherwise same reaction conditions. The results are related to the type of peroxide and also the natural, alkaline pH of the RR21 effluent changing ozone chemistry [60,61,76].

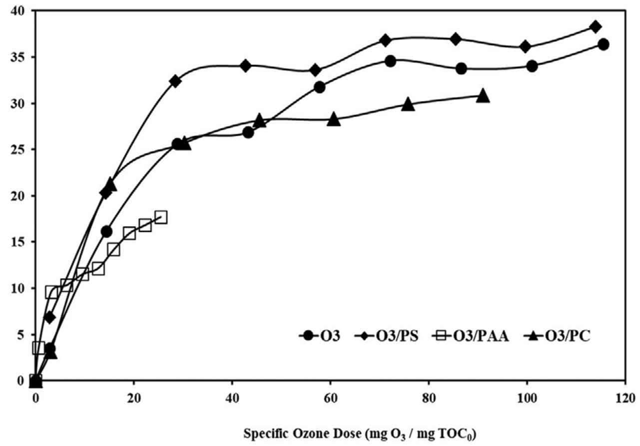


Fig. 2. Effect of the specific ozone dose (in mg O_3/mg TOC_0) on TOC removals (in %) for ozonation and O_3/peroxide treatments. Experimental conditions: Ozone feed rate=72 mg/min; ozonation time=40 min; peroxide concentration 1.5 mM; initial RR21 concentration=100 mg/L; initial TOC=25 mg/L (from 100 mg/L RR21 dye); initial TOC=113 mg/L (from 100 mg/L RR21 dye+1.5 m PAA oxidant); pH=11.0.

2. TOC Removal

TOC removals were also followed for ozonation and peroxide-assisted ozonation during 40 min treatment at an ozone feed rate of 72 mg/min in the presence of 1.5 mM peroxides, which treatment conditions were selected because these resulted in the highest color removal rates and corresponded to a peroxide : ozone stoichiometry (molar ratio) of 0.2 (mM peroxide/mM O_3), that is indicated as the theoretical optimum range for peroxide : ozone treatment processes [62-64]. Fig. 2 displays percent TOC removals obtained for the applied (specific) ozone doses (expressed in "mg O_3 absorbed per mg initial TOC") for the above-mentioned reaction conditions.

It has been demonstrated that ozone-based AOPs are more efficient than ozonation in terms of ultimate oxidation/organic carbon removal as a consequence of the free radical formation resulting in the involvement of oxidants being much stronger than ozone [36,37]. Here it should also be noted that since the initial TOC is different and higher for the O_3/PAA experiments (TOC=113 mg/L instead of 25 mg/L due to 1.5 mM PAA addition) than that of the other ozone/peroxide treatment sets, the specific ozone dose is more than four times lower than for mere ozonation and the other ozone/peroxide treatments (25 mg O_3/mg TOC_0 instead of 91-116 mg O_3/mg TOC_0). The overall TOC removals were obtained in the range of 30-40% for ozonation (in the absence of peroxide; 36%), O_3/PS (38%) and O_3/PC (31%), whereas the overall percent relative TOC removal decreased to 18% for O_3/PAA treatment due to its higher initial organic carbon content. Although there was not much difference observed among the ozone/peroxide treatment processes both in terms of color as well as TOC removals/removal rates, PS-assisted ozonation outperformed the other treatments in

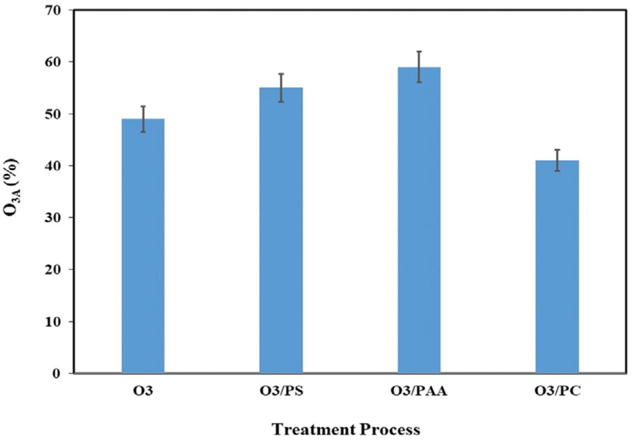


Fig. 3. Ozone absorption rates ($O_{3,A}$; in %) for ozone and O_3/peroxide (PS, PAA and PC) treatments. Experimental conditions: Ozone feed rate=72 mg/min; ozonation time=40 min; initial RR21 concentration=100 mg/L; initial TOC=25 mg/L from 100 mg/L RR21 dye; initial, total TOC=113 mg/L from 100 mg/L RR21 dye and 1.5 m PAA oxidant; pH=11.0.

terms of TOC abatements, as in the case of color removal, revealing that $SO_4^{\bullet -}$ - based treatment of RR21 effluent with ozone is the most attractive option among the studied treatment combinations.

3. Reaction Pathway for Ozone and Peroxide-Assisted Ozonation

Ozone chemistry is affected by several environmental factors such as pH, temperature and the presence of free radical initiators, promoters and scavengers present in the water and wastewater sample. The presence of scavenging chemicals (alkalinity) decreases ozone decomposition and hence increases its stability [19,23,77]. In this way, other, more selective radicals such as bicarbonate/carbonate radicals may become important in the reaction pathway [38,76]. Fig. 3 depicts percent ozone absorption rates (O_{3A} values; in %) for ozonation and selected ozone/peroxide treatments (experimental conditions: Peroxide concentration=1.5 M; ozone feed rate=72 mg/min; ozonation time=40 min). Ozone absorption rates measured for different treatment combinations indicated that in the presence of PS and PAA, ozone absorption increased from 49% (ozonation only) to 55% and 59%, respectively, which supports enhanced ozone decomposition and could be the major reason of elevated color removal rates observed during PS- and PAA-assisted ozonation. For O_3/PC, on the other hand, no increase but a decrease in ozone absorption rates to 41% was evident, speculatively due to a different oxidation pathway than the other two ozone combinations. Ozone absorption indicates enhanced ozone decomposition to less stable radicals as was expected for PS-and PAA-assisted ozonation. In the presence of PC, carbonate ions and HP are released into the reaction solution that form $CO_3^{\bullet -}$ and $HO^{\bullet}$, respectively. The high alkalinity of the reactive dyebath effluent is expected to consume/scavenge $HO^{\bullet}$; thus, a $CO_3^{\bullet -}$-dominated, slower and more selective reaction pathway is expected to become important during PC-assisted ozonation as already mentioned above.

This evidence is also supported by the liquid phase (bulk) ozone concentrations that have been measured in parallel to the ozone absorption rates for ozonation and ozone/peroxide treatments throughout ozonation. Steady-state dissolved, molecular ozone concentrations being reached after t=8-10 min (576-720 mg O_3) ozonation were determined as 5.2 mg/L (with 49% ozone absorption), 4.0 mg/L (with 55% ozone absorption), 3.1 mg/L (with 59% ozone absorption) and 5.5 mg/L (with 41% ozone absorption) for O_3, O_3/PS, O_3/PAA and O_3/PC, respectively. These bulk ozone concentrations speak for a relationship between ozone absorption and aqueous, residual ozone concentrations. Namely, the higher the ozone decomposition rates, the more ozone absorption occurs and at the same time, the dissolved, molecular ozone concentrations decrease appreciably. Thus, as expected, an inverse relationship between ozone absorption (ozone decomposition) rates (O_{3A} values) and dissolved, molecular ozone concentrations was apparent. The differences in ozone absorption and bulk dissolved ozone concentrations for different ozone/peroxide treatment combinations are most probably due to differences in ozone decomposition rates into different ROS. These deviations would affect the reaction pathway and kinetics of RR21 dyebath effluent treatment.

4. *V. fischeri* Toxicity and Biodegradability as Changes in BOD_7

To decide whether implementation of the proposed peroxide/ozone treatment system is feasible, it is important to study its ecotoxicological safety by conducting some toxicity and biodegradability tests. Previous research has reported that the application of ozonation at alkaline pH and combined ozonation processes could in some cases result in more toxic and/or less biodegradable oxidation products [57,78-81]. However, in theory, the opposite is expected; that more hydrophilic and hence more biodegradable/less toxic degradation products might form during combined treatment processes involving ozone [2,18,78]. The situation depends on the reaction conditions; that is, oxidant/catalyst concentrations, water/wastewater type, organic/inorganic composition as well as other conditions and environmental factors (presence of metals, polymeric and/or metal-complexing substances, bromide/chloride/nitro/nitroso-bearing aromatics, etc.). Therefore, in the present study, the original and ozonated samples were subjected to acute toxicity tests employing *Vibrio fischeri*. Percent relative inhibition rates for the original and treated (ozone feed rate=72 mg/min; ozonation time=the exact time/ozone dose corresponding to complete color removal and t=40 min; peroxide concentrations=0.00 and 1.5 mM pH=11.0) RR21 dyebath effluent samples are presented in Fig. 4.

From Fig. 4 it is apparent that with increasing ozone dose (and hence ozonation time), the toxicity first increased corresponding to the time of complete color removal, but thereafter decreased (here shown for ozonation at t=40 min, where TOC removal also slowed). These findings reveal that toxicity can show fluctuations due to the formation of various degradation intermediates during ozonation. However, when after some ozone dose TOC removal (representing the ultimate oxidation to some mineralization end products) starts during the later stages of treatment, the inhibitory effect (acute toxicity) is expected to decrease in parallel to TOC abatement. This is in accord with previous work where an appreciable increase followed by a serious reduction in the toxicity parameter has also been evidenced and attributed to the changes in TOC [4,18,35,82,83]. It should be pointed out here that the inhibitory values always remained below 35% revealing that the original and ozonated/perozonated reactive dyehouse effluent samples were never

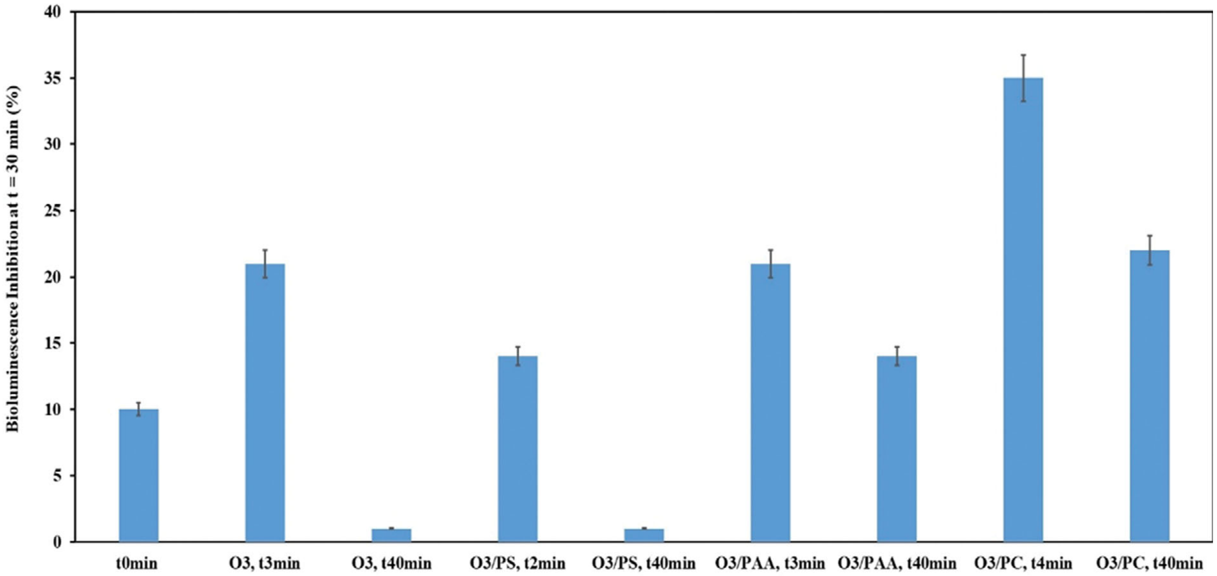


Fig. 4. Percent relative bioluminescence inhibition (*V. fischeri* incubation time=30 min) for RR21 dyebath effluent before/after ozonation and O_3/peroxide treatments. Experimental conditions: Ozone feed rate=72 mg/min; ozonation time is the i) time of complete color removal and ii) 40 min; peroxide concentration=1.5 mM; initial RR21 concentration=100 mg/L; initial TOC=25 mg/L; initial, total TOC=113 mg/L from 100 mg/L RR21 dye+1.5 mM PAA oxidant; pH=11.0.

seriously toxic. Hence, from the bioassay results it can be concluded that throughout ozonation and peroxide/ozone treatment relative inhibition values fluctuated but did not increase dramatically, which is a critical result in terms of ecotoxicological safety of a treatment system.

The BOD parameter was also followed during ozonation and peroxide-assisted ozonation of RR21 effluent. The BOD_7 values were determined as 2.5, 4.6, 3.9, 5.8 and 2.1 mg O_2/L for the original, ozonated, O_3/PS, O_3/PAA and O_3/PC-treated RR21 dyebath effluent samples, respectively, using acclimated sludge (heterotrophic biomass). These values were very low and not so meaningful for extensive interpretation; however, it is evident that the changes in the biodegradability of the reaction solution are minor and the degradation products are not more biodegradable than the original RR21 effluent sample. Note that the pH and peroxide concentrations were carefully checked prior to sample preparation and dissolved oxygen measurements, indicating that there were no interferences/errors due to the presence of peroxides or pH variations. Besides, pH buffers are always being used during BOD tests to keep the pH at a constant, neutral value. The already low organic carbon content that decreased from 25 mg/L to 17-18 mg/L TOC during treatment could be a major reason of the poor biodegradability and low BOD_7 values, though the heterotrophic biomass used as the seed source was acclimated to the sample. It was taken from the textile wastewater treatment plant's sludge waste recycle line. On the other hand, it is known that reactive dyes are recalcitrant and hence acclimation of biomass to reactive dyestuffs is typically not possible [57,80,81].

CONCLUSIONS AND RECOMMENDATIONS

The discharge of colored wastewater due to the intensive use and high concentrations of textile industry dyes reaching 1,000 mg/L in the dyebath and 100 mg/L in the ultimate dyehouse effluent continues to be a major environmental, economic and technical problem especially in developing countries. Hence, the search for more effective and at the same time ecotoxicologically safe/sustainable treatment methods to treat dyehouse effluents prior to their discharge into receiving water bodies is continuing to be a serious challenge to the textile dyer and finisher. In the present work, a simulated reactive dyebath effluent containing the commercially important fiber reactive dye RR21 and the dye assisting chemicals soda-ash (Na_2CO_3) and sodium chloride (NaCl) was subjected to ozonation and peroxide-assisted ozonation to explore the effect of alternative, "green" peroxides on the degradation of the targeted reactive dye pollutant. Changes in color (the reactive dye's peak absorbance) removal rates and TOC removals were selected as the process dependent variables for ozone and peroxide-assisted ozonation treatments. As the peroxides, persulfate (here: Peroxydisulfate; PS) and the relatively less studied alternative oxidants peracetic acid (PAA) and percarbonate (PC) were selected and added at varying concentrations (=0.75-6.00 mM) to the ozonation system. The following conclusions were drawn from the experimental study: for all studied treatment processes, complete and abrupt color removal was obtained at low ozone doses (144-288 mg O_3). In terms of color removal, PS- and PAA-assisted ozonation outperformed sole ozonation and the addition of PC inhibited both color and TOC removal due to the free radical scavenging reaction of carbonate ions with hydroxyl radicals, forming more stable and selective carbonate radicals acting as the major active oxidant of O_3/PC treatment. The highest TOC removal was observed for O_3/PS (38%), closely followed by ozonation alone at the natural, alkaline pH of the reactive dyebath effluent with 36% TOC removal (applied ozone dose=2,100-2,800 mg). Since the peroxide PAA contributed to the organic carbon content of the RR21 effluent, the relative overall TOC removals obtained for this treatment combination were relatively low (only 18%), although the addition of PAA enhanced both color and TOC removal rates (kinetics) of ozonation. O_3/PC resulted in the poorest and slowest color and TOC removal. The involvement of free radicals and free radical scavenging effects was confirmed with gas-phase (feed- and off-gas) and liquid (bulk) ozone measurements. Higher ozone absorption and decomposition rates were measured for O_3/PS and O_3/PAA treatments, which were already relatively high since ozonation was conducted at the natural, alkaline pH of the reactive dyebath effluent. Acute toxicity tests conducted with the marine photobacterium *Vibrio fischeri* indicated that the original RR21 dyebath effluent was practically non-toxic and thus exhibited a low relative inhibition rate ($\approx$10%). The acute toxicity of the reactive dyebath effluent slightly increased during O_3/PAA and O_3/PC treatments, whereas no inhibitory effect was observed for the sample after O_3/PS treatment, which finding was parallel to the higher color and TOC removal observed for this process. BOD_7 (biodegradability) measurements were also conducted and low BOD values were determined for all samples. Results indicated that in particular the PS/O_3 process appeared to be a feasible, promising treatment option for reactive dyebath effluent treatment. In case that the reactive dyebath effluent bears a variety of dye assisting chemicals (surfactants, complexing agents, soda ash, etc.), the positive effects of peroxide addition could change and differ more appreciably from mere ozonation. However, pilot-and full-scale treatability studies with real and hence more complex textile dye wastewater would be necessary to decide whether ozone/peroxide treatment is economically feasible and ecotoxicologically safer than mere ozonation at the alkaline, natural pH of dyehouse effluent.

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