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Effect of Inorganic Additives in the Textile Dyes Removal by Ozonation

Arizbeth Pérez, Tatiana Poznyak and Isaac Chairez

Additional information is available at the end of the chapter

Abstract

Treatment of industrial wastewaters based on oxidative efficiency of ozone is still of great interest due to the high removal percentages of the initial pollutants and their by-products. In particular, the industrial dyes and their wastewaters have received special attention considering the large volumes of water produced daily with high concentration of chemical oxygen demand. In addition, the dyeing processes use some chemical additives to enhance the final quality of dyeing. The effect of all these additives on the wastewater treatment has been insufficiently explored. This chapter is focused on the study of different additives commonly used in dyeing process (Na_2SO_4 and Na_2CO_3 for Reactive Black 5 – RB5, Na_2SO_4 at different concentrations for Direct Red 28 – DR28, and acetic acid for Basic Green 4 – BG4) and their effect on ozonation efficiency in discoloration and dye decomposition. Moreover, the distribution of by-products obtained throughout the ozonation was compared when the additives are or not participating in the reaction. The influence of additives and dyes' chemical nature, their concentration, and the induced pH variation on dye solutions are explained using the results of ozone based on the treatment of the three dyes mentioned earlier. The characteristics of each dye combined with the corresponding additives over degradation and decomposition efficiency by ozone, and the by-product distribution was also studied.

Keywords: Dyes, discoloration, degradation, additives, ozonation

1. Introduction

1.1. Dyes and additives regularly used in textile industry

Dyes are colored unsaturated organic molecules that have strong affinity to natural and synthetic fabrics Kas131. Dyes are physically bound to the fiber by one or more physical forces,

including hydrogen bonding, van der Waals, and ionic forces, and in certain cases chemically bound by covalent interaction Zol87.

Dyes are classified accordingly to different criteria such as color, intended use, trade name, chemical structure, and application Sar98, Per99. However, these last two options are the most widely used. Chemical structure indicates the chromophore groups in dyes, but it only designates basic structural aspects of them Teh10. This classification scheme and the major dye classes are detailed in Table 1.

Type of dye	Example of dye
Dyes containing anionic functional groups	Acid, direct, mordant, and reactive dyes
Dyes requiring chemical reaction before applications	Vat, azoic, and sulfur dyes
Dyes containing cationic groups	Basic dyes
Special colorant classes	Disperse, solvent, pigments, and natural dyes

Table 1. Classification of dyes and some examples

In this study, some examples of regular dyes were considered to prove the effect of ozone on discoloration and dye decomposition. Benzidine-based azo dyes (BBADs), such as Reactive Black 5 (RB5) and Direct Red 28 (DR28) are classical examples Kal07, Cho96, are the principal compounds in diverse industrial products and several secondary processes. BBADs correspond to about 20–30% of dyes used in the textile industry.

Dyes derived from triphenylmethane (TPM), which include Basic Red 9 (BR9), Basic Green 4 (BG4), and Basic Violet 3 (BV3), are largely used by textile industries in several dyeing practices. This collection of dyes is a primary matter in coloring plastics, gasoline, varnish, fats, oil, paper, leather, and waxes. BBA and TPM dyes are the most extended colorants used in industrial processes AnS02.

The improvement of the dyeing process requires some other chemical reagents known as auxiliaries or additives. These compounds increase the quality properties of the final product and improve the silkiness, texture, light resistance, stability, and so on. The surfactants, inorganic and organic salts, polymers, oligomers, and solubilities are compounds regularly used as additives, among others Zha04. Table 2 shows some examples of dyeing additives used in the textile industry considering the dye nature Gui.

Dye	Additive
Acid	Na_2SO_4, H_2SO_4, CH_2O_2, $C_2H_4O_2$, CH_3COONH_4, $(NH_4)_2SO_4$
Basic	CH_2O_2, $C_2H_4O_2$, $C_2H_2O_4$, $C_{76}H_{52}O_{46}$
Direct	$NaCl$, Na_2SO_4, $NaNO_2$, HCl
Reactive	$NaCl$, CON_2H_4, Na_2CO_3, P_2O_5, $Na_3P_2O_7$

Table 2. Additives used in the textile industry

1.2. Textile industry wastewater

Textile manufacturing processes consume considerable volumes of water. About 200–350 m^3 of wastewater per ton of finished products are regular volumes of textile industry where large amounts of dyes are used Pin04, Rob01. This particular type of wastewater is a complicated mixture of dyes, surfactants, inorganic and organic salts, polymers, oligomers, and stabilizing agents with other recalcitrant organics such as alcohols, aldehydes, and organic acids. All of these aforementioned compounds are used as additives in the dyeing, bleaching, scouring, and printing processes, except dyes Eco08.

Textile industry effluents contain high concentrations of toxic chemicals; high levels of biological oxygen demand (BOD, 110–5600 mg/L) and chemical oxygen demand (COD, 50–18,000 mg/L), a wide range of the pH values (2–14) and temperatures (15–70°C), a large quantity of total suspend solids (50–23,900 g/L), and a high degree of coloration Pal02, Raj06.

Despite the nature of dyes and their method of treatment, the decomposition of dyes produces different by-products that may be considered toxic to the human health and the aquatic life. BBADs have been identified as toxic compounds to aquatic life Khl10, and they are also considered as a possible source of a broad spectrum of immune suppression, respiratory, central nervous, and autoimmune diseases like leukemia, among others Wan02. The reaction of azo bonds of these dyes with different oxidants releases benzidine and other aromatic amines, which may cause adverse systemic health effects or even cancer Bey98. On the other hand, the TPM dye affects health, causing carcinogenesis, mutagenesis, teratogenesis, and respiratory infections Sha04.

2. Dyeing wastewater treatment

2.1. Regular methods of treatment for dyeing wastewater process

Dyeing wastewaters are usually treated using physical, biological, and chemical methods. In the last two decades, many results describing the physical treatment of these dyes have been presented. Adsorbents such as activated carbons, several industrial wastes, natural materials, bioadsorbents, and enhanced adsorption forces by ultrasound treatments have been described as remarkable examples of physical methods of treatment. The majority of dyes have high molecular weight and complex chemical structure. These characteristics yield to low biode-gradability of dyeing wastewater due to the mixture toxicity of compounds. A few of the aforementioned results have proven that only complex bacterial consortium can decompose partially low concentrated dye solution (less than 50 mg/L).

To overcome the low efficiency of biological treatments, different chemical oxidation methods can be applied. In particular, the so-called advanced oxidation processes (AOPs) are effective to degrade dyes in water by the destruction of double bonds in molecules associated with chromophores Gog04, Koc02, Lia97, Maj97, Per03, Rob011, Wan03.

2.2. Ozonation of dyeing wastewater

Dye degradation by the ozone oxidative capacity may proceed in two mechanisms: direct (reaction between molecular ozone and dye) and indirect (based on chemical radicals produced by the interaction between ozone and hydroxyl ions) reactions. When pH is acid, molecular ozone selectively reacts with some specific sections of organic molecules such as double bonds or aromatic systems of reactive dyes in direct reaction. When pH is above 7.0, hydroxide radicals obtained by the reaction of ozone decomposition interact with many organic compounds Poz, Poz08.

Therefore, alkaline to neutral pH of dyeing wastewater motivates the unspecific radical reaction. However, the pH of the solution may decrease as a consequence of the formation of organic acids that are common final ozonation by-products. The reaction mechanism shifts toward the selective direct oxidation. Then, mixed mechanisms appear during the reaction despite the initial pH fixed in the reactor.

Conventional ozonation is an effective method to degrade rapidly these dyes in aqueous solutions (3–5 min, under the initial dye concentrations up to 50–150 mg/L) achieving a complete discoloration and degradation of the dye solution LiB07, Poz07. However, the formation of toxic by-products generated throughout the ozonation process must be a major issue when ozonation is proposed as the main treatment of textile industry wastewaters. The final compounds formed after ozonation are less toxic (simple organic acids), while the partial mineralization is confirmed by the decrease in the total organic carbon (TOC) and COD.

2.3. Additives in the dyeing industry: their effect on wastewater treatment

The presence of additives has not been considered in most of the chemical treatments of wastewaters produced by dyeing processes from different industries. These compounds can have different effects on treatment efficiency.

Indeed, their effect on the discoloration and decomposition dynamics of dyeing wastewater in ozonation can be very strong Fei07, Mut04. Nevertheless, the effect of additives has not been well studied.

The BBADs are usually added with inorganic salts in order to stabilize the mixture, but these compounds might generate some complexes with dyes. If some salts like carbonates are considered as additives, these inorganic salts appear as radicals' scavengers. Therefore, the presence of additives can change severely the ozonation kinetics by the concentration and nature of additives.

The aims of this study can be described as follows:

a. To study the effects of a textile additive such as Na_2SO_4 and Na_2CO_3 in the ozonation of two commercial BBADs (RB5 and DR28) and acetic acid (AA) in the degradation of BG4 by ozone.

b. To explain how additives accelerate or decelerate both the discoloration and the decomposition of studied dyes by a simple kinetic study of all systems.

c. To identify and characterize the final products formed in ozonation by high-performance liquid chromatography (HPLC).

3. Materials and methods

The experimental procedure was divided into four stages. The *first stage* was developed to study the interaction between ozone and additives without dyes. These experiments were used to understand the stoichiometric relationship between ozone and additives. In *the second stage*, the effect of three additives on the discoloration and the decomposition of three dyes during ozonation was studied. In *the third stage*, the reaction's by-products were previously identified using a simple spectrophotometric analysis. On the basis of the results obtained in these three stages, a kinetic study was performed to design a simplified reaction mechanism.
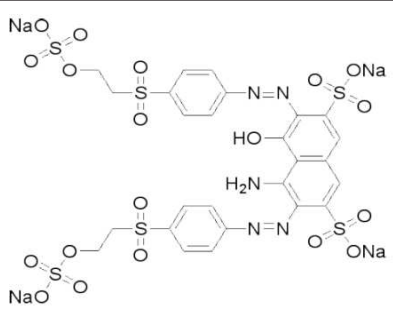
3.1. Preparation of dye solution

A set of synthetic textile dye solutions of DR28, RB5, and BG4 with concentrations of 50 and 150 mg/L dissolved in distilled water was prepared. The dyes, additives, and their concentrations to the ozonation process are summarized in Table 3.

The 50 mg/L solution was used to analyze discoloration kinetics, whereas the 150 mg/L concentration was used to identify the distribution of by-products and decomposition dynamics.

3.2. Ozonation procedure

Figure 1 shows the laboratory platform used to execute all the ozonation experiments. The temperature (23 ± 3°C) was fixed in a semi-batch reactor (batch for the liquid phase and continuous for the ozone) with a volume of 250 mL. An initial ozone concentration of 20 and 35 mg/L was selected to develop two sequences of experiments. Ozone concentrations were obtained using an ozone generator (discharge type), HTU500G ("AZCO" Industries Limited, Canada) with an oxygen flow of 0.5 L/min.

Dye concentration (50 and 150 mg/L)	Additive
Reactive Black 5	Na_2SO_4 (30 g/L), Na_2CO_3 (100 g/L); individually and in mixture

	Na$_2$SO$_4$ (10, 40, and 80 g/L)
Direct Red 28	
	CH$_3$COOH 80% (3% v)
Basic Green 4	

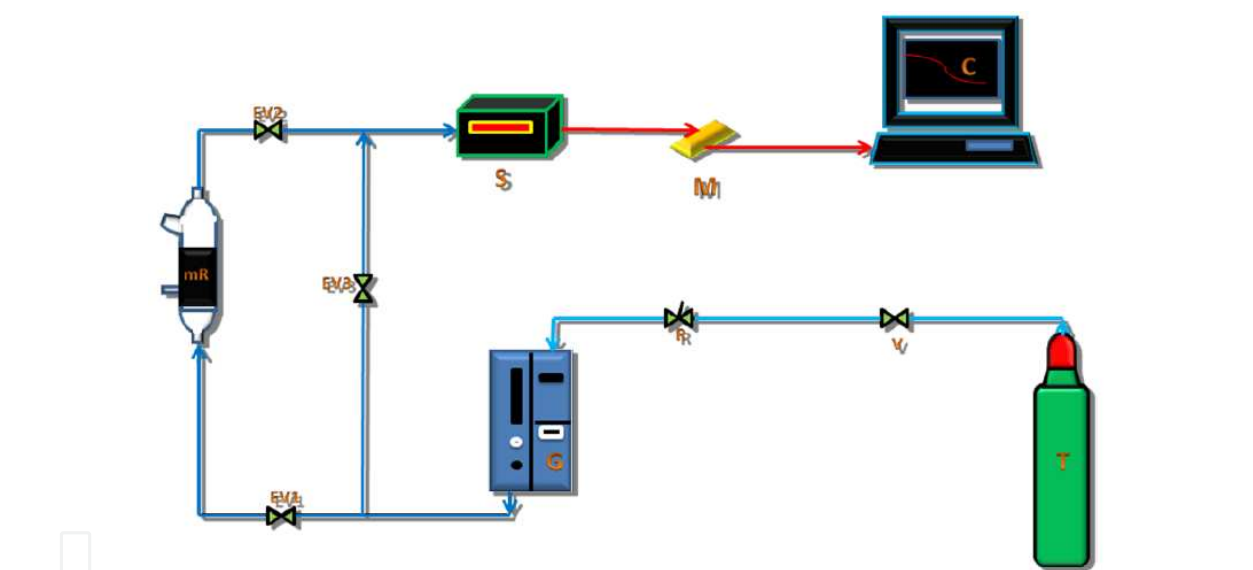**Table 3.** Determination of dye systems and additives

Figure 1. Experimental platform used to develop the ozonation: the oxygen tank (T), the ozone generator (G), the glass reactor (mR), the ozone sensor (S), the computer, the by-pass with solenoid valves (EV1, EV2, and EV3).

The ozone/oxygen mixture was distributed in the reactor using a porous ceramic diffuser located in the bottom section of the reactor. The ozone concentrations at the reactor's inlet and outlet gas streams were measured using an ozone analyzer model BMT-930, which was connected to a personal computer. Data acquisition software was used to obtain the current ozone concentration.

3.3. Analytical methods

Along the oxidation process, samples were taken at different times, which were analyzed by UV–Vis Spectrophotometer (Lambda 2B, Perkin Elmer). These samples were analyzed to

obtain the discoloration dynamics (under dye concentration of 50 mg/L) by UV–vis spectrum variation at 343 nm for DR28, 311 nm for RB5, and 250 nm for BG4. The pH variation throughout the ozonation was measured using a potentiometer (Portable pH/CON 10 and Waterproof pH/CON 10 meter, OAKTON).

The identification of by-products was performed by a HPLC analysis, (Perkin Elmer) equipped with UV–vis detector series 200 (190–360 nm) with a dye concentration of 150 ppm and an ozone concentration of 30 ppm. To obtain the dye degradation dynamics, a Platinum C18100A column (PerkinElmer, Inc.; 25034.6 mm) was used for three dyes. The mobile phase was acetonitrile–water (95:5) at 311 nm for RB5, acetonitrile–water–methanol (50:5:45) at 343 nm for DR28, and acetonitrile–water (2:98) at 250 nm for BG4. To identify the intermediates (formation and decomposition), a Spherisorb Silica column (25034.6 mm; Alltech, Nicholasville, Kentucky) was used at 255 nm. In this instance, the mobile phase was acetonitrile–water (80:20). In the case of the BG4 ozonation, the final products were identified using a column of prevail organic acid (150 × 4.6 mm, Alltech). The mobile phase was monobasic potassium phosphate 2.25 mM at pH 2.5 (for dye without additives at 211 nm) and 3.6 mM for analyzing the solution of dye complemented with AA. The HPLC analysis for all samples was performed using a sample volume of 30 μL, and the carrier flow was fixed to 0.8 mL/min.

4. Results and discussion

4.1. Additive ozonation

In order to interpret correctly, the possible interactions between the ozone dye and the ozone additive are necessary to study in each system separately. The concentrations of all additives correspond to those used in the textile industry. Table 4 shows the ozone consumption and characteristic pH to each additive solution.

Additive	Concentration (g/L)	Ozone consume (mole)	pH
Water	–	0.0075	5.6
Na_2CO_3	30	0.0263	12.4
Na_2SO_4	100	0.0067	7.8
Na_2CO_3/Na_2SO_4	30/100	0.0305	12.7
Na_2SO_4	10	0.0076	7.8
Na_2SO_4	40	0.0068	6.5
Na_2SO_4	80	0.0066	6.3
CH_3COOH (80%)	3% $_V$	0.0082	1.52

Table 4. Characteristics of additive solutions

The pH of the additive solutions has different values depending on the nature of the additive. In general, the Na_2SO_4 solutions have shown neutral pH (6.3–7.8), the Na_2CO_3 solutions have

shown basic pH (12.4), and the AA solution has shown acidic pH (1.52). The solution of the additive mixture (Na_2CO_3/Na_2SO_4) has basic pH due to the influence of the Na_2CO_3 presence.

Figure 2 shows the ozonograms of the four additive solutions in comparison with the ozone saturation in distilled water as reference. The Na_2SO_4 and the AA did not show any interaction with ozone. On the other hand, the ozonograms of the Na_2CO_3 and the salt mixture (Na_2CO_3/Na_2SO_4) solution are different to the reference with a final concentration smaller than the one used at the reactor's input. This confirms the partial ozone decomposition (about 30%) to other oxidative species.
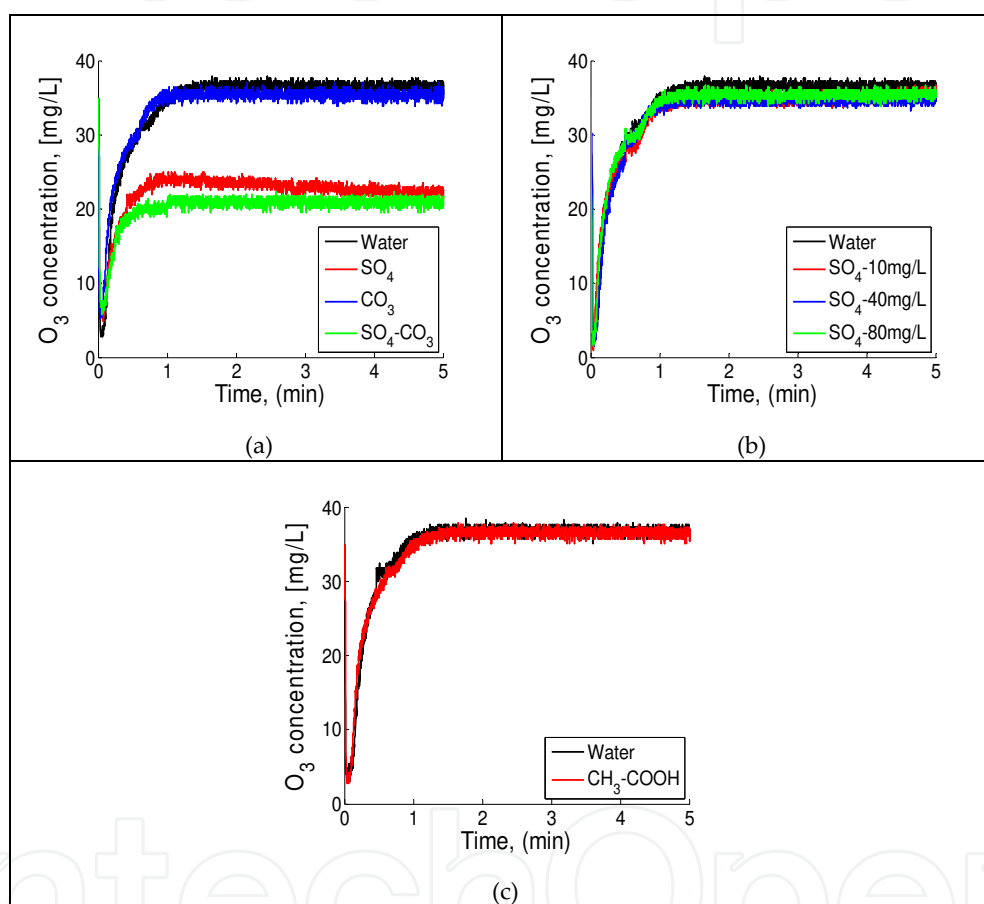

Figure 2. Ozonograms of the additives: (a) Na_2CO_3 and Na_2CO_3/Na_2SO_4, (b) Na_2SO_4 at different concentrations, and (c) CH_3COOH.

When the pH of the solution is above 7.0, the ozone decomposition promotes the formation of hydroxyl radicals. The hydroxyl radicals interacted with the carbonate ion (CO_3^{2-}), following the well-known scheme to form the carbonate ion radical ($CO_3^{\bullet-}$) that did not react with ozone but can react with dye and constitute another method of oxidation Bel05.

The difference between distilled water and sulfate solutions of ozone consumption was practically undetectable. This condition could be a consequence of the poor sulfate ions reaction with the ozone at that detected pH interval. A similar behavior was determined for

the AA solution because there is no ozone consumption. Furthermore, those kinds of compounds have lower reaction kinetic constant with ozone (10^{-3} to 10^{-1}).

4.2. Additive effect on ozonation dynamics of dyes

In general, the main parameter used to characterize the treatment efficiency of the textile wastewaters is the presence of the color and the discoloration degree. However, the removal of color does not mean that the dye was completely decomposed during the same time. In the present investigation, dye decomposition was also studied and compared with the dynamics of the color elimination by HPLC. In this case, the initial colorant concentration was 150 mg/L. To evaluate the effect of the additives on their discoloration and decomposition dynamics, the dye solutions with and without additives were ozonated at the same operation conditions. By the determination of the stoichiometry of the reaction with ozone, it is possible to propose the scheme of the decomposition mechanisms. These experiments were executed to evaluate the ozone consumption by the dye and the interactions with the additive.

Table 5 shows the stoichiometric results obtained during dye ozonation with and without additives. This relationship was determined using the total ozone consumed during the reaction and the total moles of dye. This ratio is usually called the ozone dose.

In case of RB5 added with sulfate decreased the amount of ozone consumed per mole of dye. The formation of peroxysulfate radicals can be the cause to produce this decrement. One must recall that only a portion of ozonogram is used to perform the ozone dose determination that corresponds to the expected kinetic behavior of the decomposition of the initial dye. When carbonate was the only additive for RB5, the ozone dose increased almost 20% that confirms the scavenger nature of this salts in the ozonation of dyes. Moreover, when both additives (sulfate and carbonate) were in the reaction, the ozone dose increased 33%. So, a synergic effect occurred between both additives and ozone, yielding to consume more ozone in this case.

System	Concentration (g/L)	Ozone dose (mole O_3/mole dye)
RB5	–	3.966
RB5 – Na_2SO_4	30	3.465
RB5 – $CaCO_3$	100	4.753
RB5 – Na_2SO_4 – $CaCO_3$	30/100	5.297
DR28	–	3.432
DR28 – Na_2SO_4 (10 g/L)	10	6.165
DR28 – Na_2SO_4 (40 g/L)	40	5.194
DR28 – Na_2SO_4 (80 g/L)	80	4.594
BG4	–	2.701
BG4 – CH_3COOH	3% $_V$	3.629

Table 5. Stoichiometric ratio of ozone consumed during dye decomposition

When the DR28 dye was evaluated, the ozone doses in systems with sulfate showed an inverse relation with the additive concentration. This means that 80 mg/L of ozone consumption was 74% smaller than the result obtained when the additive concentration was fixed at 10 mg/L. Nevertheless, despite the additive concentration, the ozone dose was higher than the case when there was no additive in the reaction. The BG4 ozonation is carried out in the presence of AA as additive; it was shown that the acid presence has a significant effect on the ozone consumption being 34% higher than the additive and dye solutions, this may be by the interactions between the additive and the dye generating some kind of chemical complexes.

As a preliminary conclusion, the presence of additives increased ozone consumption because the ozone decomposes itself to another compound as hydroxyl radicals or reacts with the ions from the additives to generate new oxidative species.
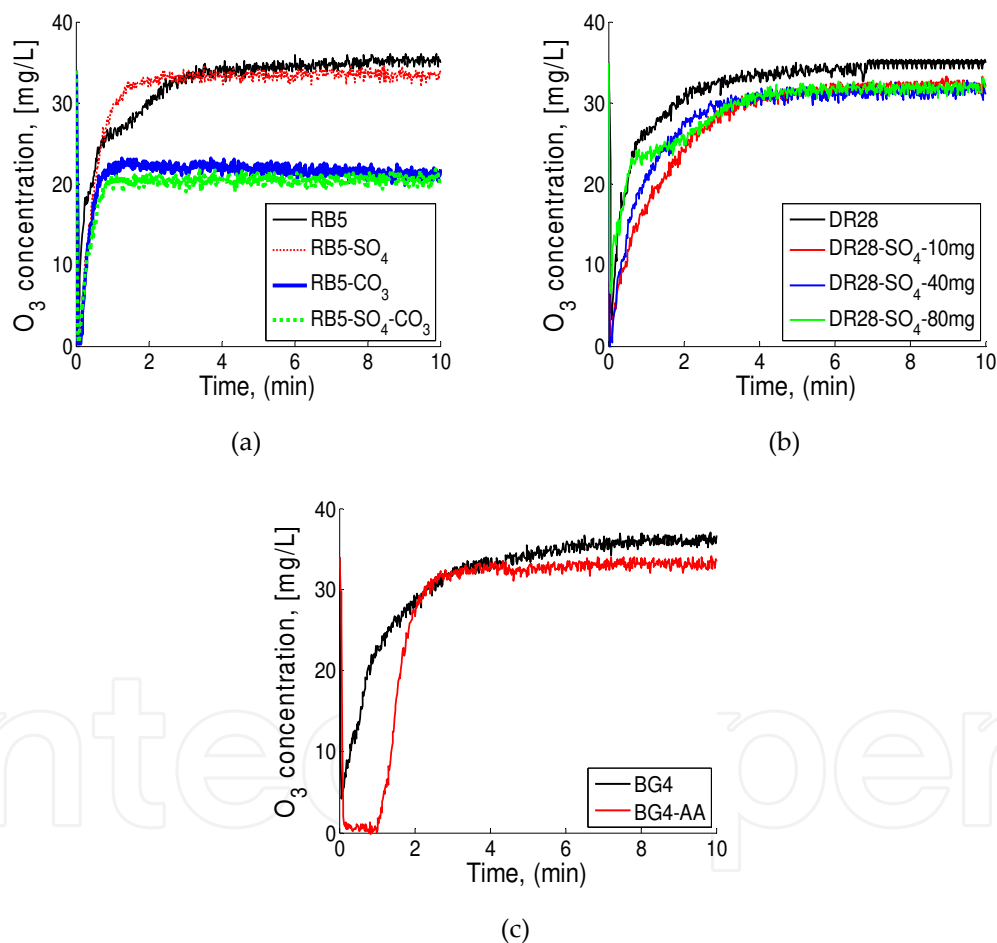

(a)

(b)

(c)

Figure 3. Discoloration dynamics of the three dyes with and without additives

4.3. Effect of additives on pH variation

Different studies Poz07,Fei07 have proven that pH decreases along the ozonation. This fact has been explained considering that initial molecule decomposition yields to organic acid such

as oxalic, formic, maleic, and so on, which triggers the acid pH. Table 6 shows the pH variation of all ozonation with and without additives.

In particular, when additives were in the reactor and the initial pH was basic, the final pH of solutions remained alkaline. This is a remarkable consequence of additives that brings a basic pH, while the concentration of organic acids generated in the ozonation reaction is not enough to force the decrement of this parameter. So, the buffer capacity promoted by additives (in the case of inorganic salts) modifies the reaction mechanism. Moreover, the null variation of pH observed when carbonate was in the reactor can obey a different process where carbonate served as scavenger of free radicals. Finally, when AA was considered as additive, pH did not vary because initial pH was already strongly acid (2.8). The poor variation of pH can be a consequence of the different pK_a of all other organic acids that are higher than the pH fixed at the beginning of the reaction.

Dye	pH initial	pH final
RB5	5.5	3
RB5 – Na^2SO^4	7	9.5
RB5 – $CaCO^3$	11	11
RB5 – Na_2SO_4 – $CaCO_3$	11	11
DR28	7.8	4
DR28 – Na_2SO_4 (10 g/L)	11	11
DR28 – Na_2SO_4 (40 g/L)	7.8	4
DR28 – Na_2SO_4 (80 g/L)	7.8	4
BG4	4	3
BG4 – CH_3COOH	2.8	3

Table 6. Average variation of pH determined in ozonation experiments with and without additives

4.4. Additive effect on dye solution discoloration and decomposition dynamics by ozone oxidative activity

4.4.1. Discoloration dynamics

According some researchers Zha04,Wan03,LiB07, the first stage in ozone reaction with dye is the attack to the chromophore groups that give the color properties to the molecule.

In order to follow the presence of chromophore groups through ozonation process, the UV–vis spectroscopy was used at each dye's characteristic wavelength: 311 nm for RB5, 343 nm for DR28, and 250 nm for BG4. Table 7 contains the information of the total time discoloration for each ozonation system when the dye initial concentration was 50 mg/L.

In case of RB5, the discoloration process was faster when the mixture of additives participated in the ozonation. The total discoloration time was reduced about 90% when compared with

the case with no additives. This percentage decreased to 82.5% when only the carbonate was used as additive.

Treatment system	Discoloration time (min)	Discoloration (k, L/mol s)	Decomposition time	Decomposition (k, L/mol s)
NR5	4.0	3.51×10^4	5.0	0.0335×10^4
NR5 – Na$_2$CO$_3$	0.75	0.140×10^4	3.0	0.0858×10^4
NR5 – Na$_2$SO$_4$	0.75	0.502×10^4	0.75	0.176×10^4
NR5 – Na$_2$SO$_4$/Na$_2$CO$_3$	0.5	42.9×10^4	6.0	0.0682×10^4
RD28	3.0	5.68×10^4	15	0.0201×10^4
RD28 – Na$_2$SO$_4$ (10 g/L)	1.0	1.07×10^4	6.0	0.0987×10^4
RD28 – Na$_2$SO$_4$ (40 g/L)	4.0	1.70×10^4	6.0	0.0897×10^4
RD28 – Na$_2$SO$_4$ (80 g/L)	5.0	0.63×10^4	6.0	0.0395×10^4
VB4	2.0	3.02×10^4	1.0	0.0813×10^4
VB4 – CH$_3$COOH	1.0	9.6×10^4	15	1.37×10^4

Table 7. Summary of discoloration and decomposition dynamics including reaction periods of time as well as the pseudo-monomolecular kinetic reaction rate constants

If sulfate was the additive to the dye solution, the percentage reduction of discoloration time was equal (82.5%). This can be explained considering that some by-products such as hydroquinone or catechol bring some kind of coloration to the solution.

In the case of DR28 ozonation without additives, the discoloration was observed after 3 min of the reaction; however, when sulfate was added with a concentration of 10 gm/L, this time decreased more than 65%.

When the additive concentration increased, the discoloration times also increased. This condition can be a consequence of the solution pH that was fixed to 11.0 and that may yield to increase in the hydroxyl radicals' formation, which in turn promotes the peroxysulfate radical (2.01 V) development accelerating dye solution discoloration. The formation of mechanisms was explained in reference.

At alkaline pH, the ozone decomposes itself to hydroxyl radicals, which can react with sulfate ions, originating the peroxysulphate ions which due to its oxidative nature (2.01 V) attacks the dye molecule in different positions resulting in its faster fragmentation [32].

The AA does not represent a significant effect on discoloration time because in both systems the same efficacy (95%) was observed in the first minute.

Some reaction mechanisms described a feasible reaction scheme of RR22 decomposition when the peroxysulfate radical appears in the reactor [39]. According to this scheme, there are two possible stages when the dye can be decomposed. The first considers the interaction with the

chromophore group where possible links may be formed by the interactions of additives or ions. The second one involves the complete molecule decomposition generating some by-products and finally some short-chain acids. In ozonation, this scheme confirms that the complete reaction did not yield to complete mineralization.

4.4.2. Decomposition time

Actually, the main parameter used to characterize the efficacy of wastewater treatment from the dyeing process is the discoloration time; however, this does not mean that total dye decomposition may occur at that stage. So, it is necessary to study this part of the reaction in order to characterize the total time decomposition with and without the additive presence.

Table 6 also presents the total decomposition time, where it has been proved that the additive presence has a strong effect on this parameter depending on the additive and the dye under analysis. A set of HPLC studies were carried out to study the decomposition of the dye molecule. These analyses were executed considering an initial dye concentration of 15 mg/L.

When the ozonation of RB5 without additives was evaluated, a decomposition efficiency of 90% was reached after 5 min of reaction. When additives participated in the reaction (individually), this efficiency was reached before 1 min of the reaction and 3 min when the corresponding additives were mixed. This time decreased when additives were in the reactor due to the presence of diverse oxidative ions that accelerated dye molecule decomposition. The same effect was observed in the case of DR28 dye where the decomposition time decreased from 15 min to 6 min. At that reaction time, a 60% of decomposition in the first reaction minute was observed.

If the BG4 dye was ozonation, the presence of the AA increased in the degradation time. Under these conditions, 90% of degradation after 15 min of the reaction was achieved when compared with the dye without additive where the same efficiency was reached before 1 min of reaction.

Discoloration and decomposition times were reduced under the presence of additives enhancing the respective efficiencies in the cases of RB5 and DR28 systems. However, BG4 does not have the same behavior.

4.5. Discoloration and decomposition kinetics

According to some researchers WYu06, Lop07,HSh06, WZh06, MSL07, the study of reaction kinetics was made based on discoloration dynamics, using an equation of pseudo-first order. The following equation was used to determine the reaction kinetic constant.

The model used to characterize either discoloration or decomposition during the dye ozonation has the mathematical structure given by:

$$\frac{dDye(t)}{dt} = -k_r Dye(t)O_3(t),$$ (1)

where k_r, the reaction rate, is constant associated to the viscosity changes, $Dye(t)$ is the variation of either discoloration or decomposition during ozonation, and $O_3(t)$ is the calculated dissolved ozone concentration measured indirectly by the ozonogram.

The model described by Equation (1) is linear with respect to their corresponding parameters. However, the model has as an independent variable the time derivative of the variable under modeling analysis. This situation complicates the parametric characterization of the reaction proposed to model the effect of ozone on these two variables.

The solution of the parametric identification problem that is to get k_r can be obtained by the application of a robust exact differentiator. This differentiator can be implemented by the super-twisting algorithm. So, consider that the signal $f(t)$ to be differentiated satisfies $|\dot{f}(t)| < f^+$, $\forall\, t > 0$. Hence, the super-twisting algorithm obeys the following structure:

$$\dot{z}_1(t) = v(t) = z_2(t) - \lambda_1 \left| z_1(t) - f(t) \right|^{1/2} \texttt{sign}\left(z_1(t) - f(t) \right)$$
$$\dot{z}_2(t) = -\lambda_2 \texttt{sign}\left(z_1(t) - f(t) \right) \tag{2}$$

A sufficient condition to recover the differentiation of function $f(t)$ is to select λ_1, $\lambda_2 > 0$. As an example, under the condition proposed to the gains, the model presented in Equation (1) can be represented as follows:

$$y(t) = -k_r x(t) O_3(t) + \varepsilon(t), \tag{3}$$

where the variable $y(t)$ is the approximation of the time derivative of the variable under analysis. The term $\varepsilon(t)$ describes the approximation error produced by the implementation of the differentiator.

The parametric identification problem presented in Equation (3) can be solved by the well-known least mean square method. This method cannot be applied directly because the signals of $x(t)$ and $O_3(t)$ are measured with different sampling times. Therefore, an interpolation algorithm was applied to homogenize the number of samples that can be used in the parametric identification method. The interpolation algorithm used an approximation based on third-order polynomials (cubic). The interpolation algorithm used the interpolation based on ozonogram. The same algorithm was applied to characterize both the double-bond dynamics and the color or dye concentration variation. The constants obtained by this method were summarized in Table 7.

4.6. By-product distribution in dye wastewater treated by ozone with and without additives

Several studies have reported that the final compounds formed by the reaction between dyes and ozone, which are short-chain organic acids, without reaching full mineralization due to those compounds have low reactivity with the ozone.

Table 8 shows the final compounds identified by the HPLC technique and their respective concentrations. Oxalic, formic, fumaric, and maleic acids where the principal compounds identified being oxalic acid that has a higher accumulation (40–120 mg/L).

System	By-product	Concentration (mg/L)
RB5	Oxalic acid	4
	Formic acid	50
RB5 – Na_2SO_4	Oxalic acid	50
	Maleic acid	Traces
RB5 – Na_2CO_3	Maleic acid	Traces
	Fumaric acid	Traces
	Oxalic acid	100
RB5 – Na_2SO_4 – Na_2CO_3	Maleic acid	Traces
	Fumaric acid	Traces
	Oxalic acid	Traces
DR28	Fumaric acid	Traces
	Maleic acid	Traces
	Oxalic acid	10
	Formic acid	40
DR28 – Na_2SO_4 (10 g/L)	Oxalic acid	120
DR28 – Na_2SO_4 (40 g/L)	Oxalic acid	80
DR28 – Na_2SO_4 (80 g/L)	Oxalic acid	50
BG4	Maleic acid	Traces
	Oxalic acid	18
	Formic acid	20
BG4 – CH_3COOH	Maleic acid	Traces
	Oxalic acid	50
	Formic acid	Traces

Table 8. Composition and the concentrations of main products formed in ozonation

So, in the case of DR28 ozonation, the fumaric (traces), maleic (traces), oxalic (10 mg/L), and formic (40 mg/L) acids were identified. The presence of the last acid attributes to the partial decomposition of oxalic acid. However, in the presence of additives, only oxalic acid was formed (50–120 mg/L), and its concentration was inversely proportional to the sodium sulfate concentration. In addition, the additive has a significant effect on the formation dynamics of the acid.

When RB5 was ozonated, the concentrations of organic acids changed in the presence of additives. So, without additives, 50 mg/L of formic acids and 4 mg/L of oxalic acid were detected. With sodium carbonate, the content of oxalic acid increased up to 100 mg/L, and in the presence of sodium sulfate, the oxalic acid concentration was 80 mg/L. In the system with the salt mixture, practically, organic acids are not observed (traces). This fact is attributed to the summary effect of the hydroxyl and sulfate radicals, and the peroxysulfate ions formed, which provokes, practically, the complete mineralization of acids.

During BG4 ozonation, several organic acids were generated, such as maleic, oxalic, and formic acids (0.3, 18.0, and 20.0 mg/L, respectively). In the presence of AA, the oxalic acid concentra-

tion was increased to 50 ppm. In particular, the AA has a significant effect on acid accumulation. This effect is negative.

5. Conclusions

Ozonation is an efficient process for the treatment of textile wastewater that has been proven through the studies of discoloration and decomposition of RB5, RD28, and BG4 without and with salt and organic acid additives.

The effect of additives on ozonation dynamics of salts and acids without dye could be observed because of OH8 formed by the ozone decomposition reaction. These radicals likely react with salt ions of additives (and) with the formation of some reactive species that serve as oxidizing agents in the reaction. In the presence of additives, pH was modified (for the systems of RB5/Na_2SO_4, Na_2CO_3, and RB5/Na_2CO_3), and the sodium carbonate effect was strong. AA did not react with ozone, but it increased the discoloration and the decomposition initial rates of BG4. This was confirmed by the comparison of the values of the reaction rate constants with and without additives.

Maleic, oxalic, and formic acids were formed in dye ozonation, and the presence of the additive increased their concentration except for formic acid.

Actually, the pH remained constant through the reaction. Carbonate stabilizes pH, and, very probably, it serves as a buffer. The presence of additives increases the discoloration and the decomposition rate of dyes studied. This was confirmed by comparing the values of the reaction rate constants with and without additives. In dye ozonation, fumaric, maleic, oxalic, and formic acids were formed, and the presence of additives increased their concentration in all systems studied. A plausible and possible mechanism for each dye was proposed based on the results achieved in this study and those reported in different preliminary studies.

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