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Chemical and Tinctorial Aspects Related to the Reuse of Effluents Treated by Ozonation in Dyeing Processes

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Abstract

The purpose of this chapter is to study the interactions that are established between inorganic auxiliaries and the by-products of contaminants present in effluents coming from dyeing operations during oxidation treatment processes using ozone, and the influence of auxiliaries and by-products on the behavior of dyes in subsequent dyeing processes using the treated water. Carrying the treatment until the complete elimination of the contaminants present in it is a very expensive operation. Because of this, it is chosen to discolor and reuse the spent dyebaths treated as many times as possible to take advantage of the water and the inorganic salts contained therein. The variable composition of the dyebaths involves kinetic aspects during the treatment, which is important to take into account in the design of the process. Various by-products are already generated from the beginning of the treatment, which will have an influence on the following stages of the same treatment process, as well as on the kinetics of the dyeing processes carried out using the treated water and on the results obtained in such dyeing processes. All this will depend on the chemical and dyeing class to which the dyes used during the subsequent dyeing processes belong.

Keywords: water reuse, oxidation, ozone, textile, dyes

1. Introduction

In order to demonstrate the influence of the mentioned auxiliaries and by-products on the dyeing processes carried out using treated water, this chapter is focused on the discoloration of aqueous solutions of two reactive dyes of wide application in the textile industry, Reactive Blue 160 (RB160) and Reactive Red 141 (RR141), through the application of ozone, with the purpose of reusing treated water in dyeing processes of cotton goods, taking advantage of the large quantities of inorganic salts contained in a spent dyebath.

The greatest water consumption in a textile plant occurs in the finishing areas, since the processes carried out there use substances in aqueous solution to modify the characteristics of the processed articles, being the main one of these characteristics the coloration. Reactive type dyes have been used since 1956 for the dyeing of articles that have a high resistance to deterioration by conventional washing, since

they are compounds that react to form covalent bond dye fiber [1, 2]. This type of resistance is known as washing fastness. However, reactive dye groups that do not react with the textile substrate are hydrolyzed during the dyeing process, which, in addition to drastically reducing the dye's performance during dyeing and increasing the amount of residual dye, precludes its reuse by reconstitution of the dyeing bath and causes them to be discarded directly to the effluent. A part of the dye (up to 50%) is hydrolyzed during dyeing. This dye is an important source of contamination and makes the reuse of water impossible [3].

Within the category of reactive dyes, the azoic type represents more than 95% of the existing structures in the most used color shades. In dyes of this kind, the color originates from nitrogen-nitrogen double bonds or azo bonds ($-N=N-$). In general terms, this is the chromophore group (color generator) most frequently used. The main field of application of reactive dyes is the dyeing of articles made of textile fibers derived from cellulose. Its application on woolen articles is more limited, since this last fiber presents good washing fastness when it is dyed with another type of higher-performance dyes, such as, for example, acid dyes [4].

For the elimination of dyes present in wastewater from the textile industry, various processes have been used, both physical and chemical, as well as biological processes. However, reactive dyes are toxic compounds that are difficult to eliminate by biodegradation or separation methods, such as membrane filtration, coagulation-flocculation, or adsorption on activated carbon. The elimination of the color of a wastewater of this type can be carried out to comply with the environmental norms in the discharges, or else, in order to reuse the water. Both in the case of the treatment with activated carbon and in the coagulation-flocculation, results of color removal are obtained just over 50%, which are insufficient for any of the mentioned objectives [5].

Regarding the elimination of color to reuse water, very remarkable results have been achieved, close to 100%, through the use of nanofiltration membranes. However, this method does not solve the problem; it only separates the contaminant, without eliminating it. On the other hand, it presents technical difficulties, in terms of the difference in pressure due to the occlusion of the membranes, which causes its deterioration, in addition to the disposition of the separated contaminant. In the same way, chemical methods, particularly oxidation, have been used to eliminate the dyes present in wastewater in order to reuse it. The best results in terms of complete elimination of the dye until its mineralization have been obtained by photocatalysis, either homogeneous (photo-Fenton processes) or heterogeneous (using semiconductors, especially TiO_2) [6].

The ozonation, on the other hand, has been used individually, combined with hydrogen peroxide (peroxonous), as well as in conjunction with the application of UV radiation or the presence of activated carbon, and various combinations of these methods. This type of combination, as well as photocatalytic and Fenton processes, is known as advanced oxidation processes (AOPs) [6].

Ozone is an oxidant that does not generate its own waste; this allows obtaining a treated water with suitable characteristics to be used in dyeing processes of textile materials. In addition, the use of ozone individually enables a better understanding of the oxidation process, by avoiding interferences due to the contributions of the processes involved in the combined methods [7].

The dyes were selected for study because they are among the highest consumption by the textile industry. On the other hand, these compounds belong to one of the groups of dyes that are used more frequently: RB160 and RR141 are monochlorotriazinic reactive dyes, considered as moderate reactive and dyed at temperatures of 80°C [8].

In this study, the partial oxidation of the dyes is verified, since the complete mineralization of these products by ozonation is an extremely long process, which greatly increases the cost of a process of this type and, consequently, is not the most frequent form of work in real water treatment systems.

The oxidation of the dye implies that the treated water, at the end of the process, contains intermediate oxidation products. In the case of the reuse of water treated in dyeing processes, it is necessary to verify that such by-products do not interfere with the results obtained in terms of dyeing quality. For this purpose, dyeing tests were carried out in the laboratory with two of the most frequently used dye classes for dyeing cellulosic fibers: direct dyes and reactive dyes. These tests were evaluated by a standard procedure used in the production areas of the textile industry to evaluate dyeing results compared against a reference standard or sample to match.

For the dyeing tests, a common trichromy of reactive dyes was used, that is, the cotton samples were dyed using Reactive Yellow 84 (RY84), Reactive Red 141 (RR141), and Reactive Black 5 (RB5), separately. While in the case of dyeing with direct dyes, a trichromy consisting of Direct Yellow 50 (DY50), Direct Red 23 (DR23), and Direct Blue 80 (DB80) was used. This trichromy of direct dyes was chosen because, like the three reactive dyes under study, they cover a wide range of tones and also cover the three categories of direct dye classification established by the Society of Dyers and Colourists (SDC), which is the broadest usage classification [8].

The results obtained show that the discoloration of the compounds studied is rapid even at very low concentrations of ozone, as is the case of the concentration used in this study. However, the decomposition of dyes is a much longer process and, in fact, is not carried out with ozone even using it for long periods of time at low concentrations.

The initial concentration of dye has a marked influence on the reaction rate, sharply changing the kinetics of discoloration within the range of concentrations studied. Likewise, the presence of chemical auxiliaries has a more pronounced influence at low concentrations, because at high concentrations the aggregation of the dyes increases, influencing the kinetics [1].

The ozone applied to the discoloration of the compounds studied does not negatively influence the concentration of sodium ion present in the solution but rather increases it slightly. This situation is important because the sodium ion is necessary to carry out the process of dyeing the treated water.

Within a limited range of cycles, the quality of the dyeing obtained using water treated by ozonation complies with the specifications of the method used in industry, called AATCC 173-2005 Calculation of Small Color Differences for Acceptability, established by the American Association of Textile Chemists and Colorists [9].

The influence of the by-products formed from each dye during the ozonation in the subsequent dyeing depends on the category of dye used to dye the goods, in this case of mercerized cotton. It is more pronounced for dyeing with reactive dyes.

Through the treatment scheme used in this work, it is possible to eliminate the dyes contained in the wastewater for a very short time (10 min), using very low concentrations of ozone (2 mg/L). The kinetics of the process depend on the chemical constitution of the dye and on the residual water variables such as the initial concentration of dye and dyeing auxiliaries. The ozonation allows to reuse the treated water in dyeing processes with direct dyes and reactive dyes for up to four cycles, depending on the type of dye used. The by-products resulting from simple ozonation accumulate during the cycles of reuse without significantly affecting the quality of the resulting dyeing and can be converted into biodegradable substances by a longer ozonation. **Figure 1** shows the chemical structures of RB160 and **Figure 2** shows the chemical structure of RR141.

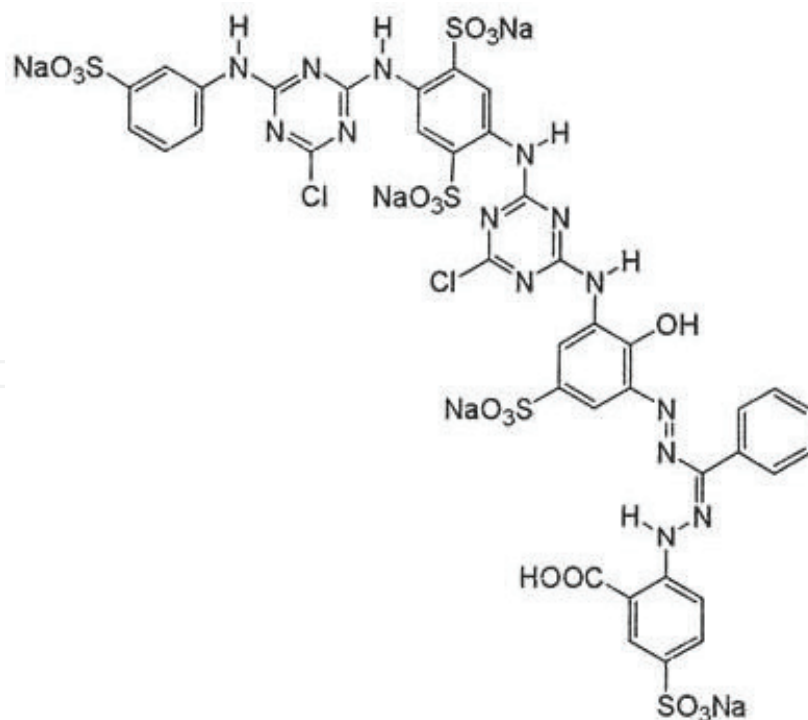


Figure 1.
Chemical structure of Reactive Blue 160 (RB160).

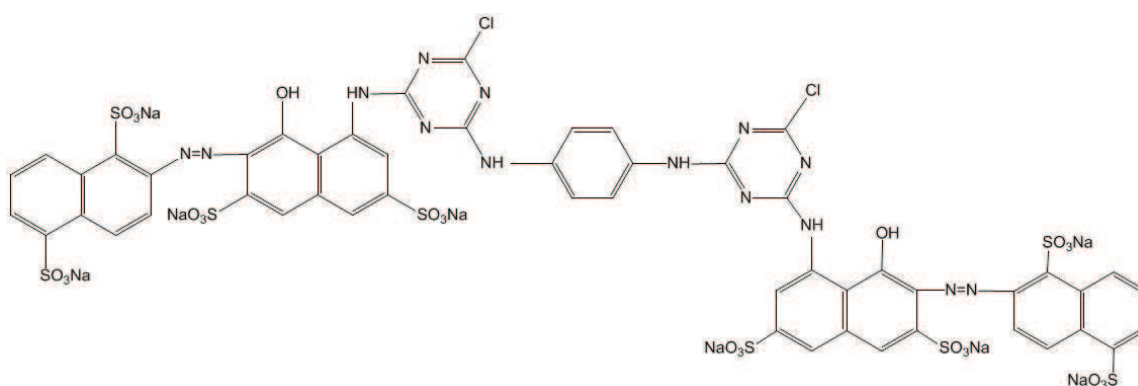


Figure 2.
Chemical structure of Reactive Red 141 (RR141).

2. Methodology

The dyes were studied individually, varying their initial concentration and varying inorganic chemical auxiliaries to simulate a dyeing effluent. Industrial samples of the three dyes were used, without any further purification. The supplier was Sinochem Ningbo, which is one of the largest presences in the Mexican market.

2.1 Ozone production

The ozone was obtained from dry air, using a corona type discharge generator (Peak Corporation). For the analysis by FTIR spectroscopy, ozone was obtained using the same generator, fed with pure oxygen (99.5%, Infra). The ozone concentration was analyzed at the output of the generator with a BMT201 (BMT Messtechnik).

2.2 Ozone reactor

The ozonation experiments were carried out in a semicontinuous glass reactor of 500 mL capacity. The reactor has an entrance in the lower part where the O_2/O_3 gaseous mixture is injected; this mixture ascends passing through a porous silica plate diffuser that evenly distributes the ozone bubbles in the liquid phase, ensuring that these are as small as possible to achieve a better mass transfer [10]. The reactor also has an outlet at the top for the ozone that does not participate in the reaction. Also, the reactor has a side key in the lower part to sample the ozone solution.

2.3 Experimental procedure

Initially, a model solution of 50 mg/L concentration was prepared for each dye. This concentration is within the range of concentrations regularly found in the effluents of the textile industry [5]. Subsequently, concentrations of 100 and 150 mg/L were used to study the effect of the concentration on the kinetics of the reaction, and solutions of 5 g/L, to carry out a preliminary analysis by FTIR.

The ozonation experiments were carried out on 400 mL of each model solution in the 500 mL reactor, with 2 mg/L of initial ozone concentration and a gaseous mixture flow (O_3/O_2) of 500 mL/min, at room temperature (20–25°C). The maximum ozonation time was 120 min. Samples were taken every 10 min and, in some cases, every 5 min.

Preparation cycles of the model solution and ozonation were made for 10 min, up to five times, with 50 mg/L solutions under the described conditions. That is, the sample solution of dye was prepared at 50 mg/L, and the ozone treatment was applied for 10 min; after this, the same sample was reconstituted with a concentration of 50 mg/L of textile dye, and it was treated again with ozone for 10 min. This cycle of contamination-discoloration was repeated up to five times with each textile dye, so that at the end there was a series of five samples of 400 mL, for each dye. The first sample had been subjected to a single cycle, the second sample to two cycles, the third sample to three, and so on until completing the five cycles. The purpose of this part of the work was to represent the recirculation of water within the process.

These samples were used for dyeing tests of textile material with reactive dyes and direct dyes. For the dyeing with reactive dyes, Reactive Black 5 (RB5), Reactive Yellow 84 (RY84), and Reactive Red (RR141) were used, while for dyes with direct dyes, a trichromy composed of Direct Yellow 50 (DY50), Direct Blue 80 (DB80), and Direct Red 23 (DR23) was selected. The dyes were carried out in a closed machine with infrared heating (Mathis). The DY50 corresponds to group A of the SDC classification of direct dyes (self-regulating); DB80, group B (controllable by means of salt); and DR23, group C (controllable by means of salt and temperature). The color difference was measured with respect to control samples, dyed with distilled water by reflectance spectrophotocolorimetry.

A second series of samples was prepared in the manner described in the previous paragraph, adding from the first cycle the equivalent to 50 mg/L of sodium ion. This was carried out in order to verify their presence throughout the ozonation cycles, using atomic absorption spectroscopy.

2.4 Analytic methods

2.4.1 pH and conductivity measurement

The variation of the pH during the ozonation was measured with a Jenway pH meter model 3310 equipment. Likewise, the variation of conductivity was

measured, in order to indirectly determine the formation of ionic species. The latter was used as a criterion to verify the separation of the groups capable of forming ions, located in the molecules of the dyes, during the ozonation process.

2.4.2 UV-Vis spectroscopy

Preliminary information about the discoloration and decomposition of textile dyes in water was obtained from the variation of absorbance in the UV-Vis range, between 190 and 700 nm, with a Cary 50 (Varian) spectrophotometer. The discoloration of RR141 was analyzed at 544 nm and discoloration of RB160 at 615 nm. Similarly, the degradation of RR141 was analyzed at 288 nm, and the degradation of RB160 at 280 nm. These wavelengths correspond to the absorbance maxima of the compounds studied within the visible and UV ranges, respectively.

2.4.3 FTIR spectroscopy

An FTIR analysis was carried out to obtain information about the functional groups that are formed and disappear in the course of ozonation. For this purpose, a PerkinElmer Series 200 equipment was used. The samples of dye subjected to ozonation at intervals of 4 h, up to a maximum of 12 h, were dried and prepared in the form of a tablet mixed with KBr, to effect the measurements.

2.4.4 Atomic absorption spectroscopy

Sodium ion monitoring was carried out through the ozonation cycles of the samples prepared for dyeing, using an AA3300 spectrophotometer (PerkinElmer). The purpose of this analysis was to directly verify that ozonation did not have any adverse effect on the inorganic salt content necessary for subsequent dyeing.

2.4.5 Reflectance spectrophotocolorimetry

With the series of samples of model solutions of 50 mg/L of concentration at which the cycles of contamination with dye and subsequent ozonation were carried out up to five times, dyeing tests were made with reactive and direct dyes applied on samples of cotton, for determining the feasibility of reusing water pretreated with ozone in dyeing processes of cellulosic materials. The dyes were made on cloth prepared for this purpose. A dyeing was made with each water sample, and the difference in color kept by the samples of cloth dyed with the pretreated water was determined in relation to a reference standard, that is, a sample of the same type dyed using distilled water and maintaining the other constant conditions. The test was carried out according to the AATCC method 173-2005 of the American Association of Textile Chemists and Colorists (AATCC) called Calculation of Small Color Differences for Acceptability, which is of extended application in the textile industry [9].

A Color Eye 7000-A spectrophotometer (Gretag-Macbeth) with color integration sphere and colorimetry software was used. This equipment simulates the color appreciation by the human eye and translates it into a value or coefficient of color difference (ΔE) that, according to the method used, should not be greater than unity, that is, $\Delta E < 1.0$. This value less than 1.0 represents a color difference that a common observer could not perceive, while $\Delta E > 1.0$ is a color difference that any person can detect and, therefore, implies that the result of a dye is not acceptable [9].

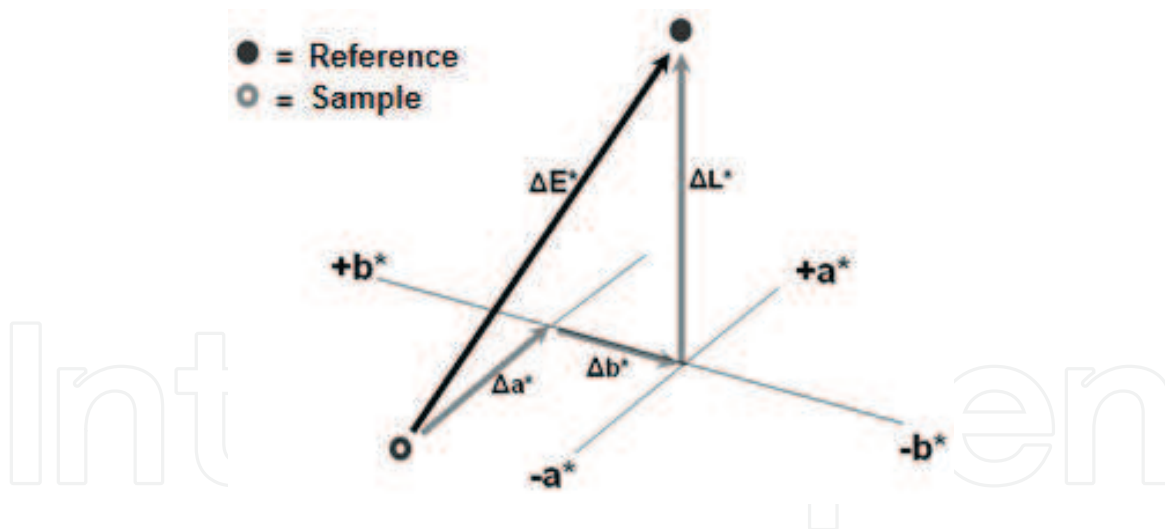


Figure 3.
 Graphic representation of color difference, ΔE .

The principle on which the method of determination is based is of a psychophysiological nature and is known as Young's Theory. It refers to the fact that the human eye perceives color through three types of receptors and considers the sensory response as inscribed in a Cartesian space, where the axis L corresponds to the opposite pair black-white ($-L$ corresponds to the color black and $+L$ corresponds to the color white), the axis a corresponds to the pair green-red ($-a$ corresponds to green and $+a$ to red color), and the b axis corresponds to the yellow-blue pair ($-b$ corresponds to blue and $+b$ to yellow).

It is considered that each color tonality constitutes a point in the color space, and the color difference between two samples is calculated as the distance between the two points that represent the tonalities of the two samples compared, considering one of them as the standard. In this way, the color difference translates into a single numerical value that allows us to easily handle it. **Figure 3** illustrates a color difference between two samples (ΔE) within the color space.

3. Results

In all cases, the discoloration was carried out during the first hour, despite the low concentration of ozone used. The addition of inorganic auxiliaries accelerates the reaction of ozone with textile dyes. **Figure 4** presents the variation of the UV-Vis spectra for the RR141 during 60 min of ozonation. From the variation of the spectra of the RR141 dye during ozonation, it can be concluded that this compound is rapidly destroyed under the action of ozone. The tendency to discoloration during the ozonation process is very similar for both dyes. The studied compounds are rapidly destroyed under the action of ozone. **Figure 5** shows the discoloration of RB160 for three different concentrations at 615 nm.

The influence of the by-products of the degradation of the dyes on the dyes made with the treated water depends not only on the accumulation of these through the cycles of ozonation contamination but also of the dyeing class of the dye used in the dyeing with the treated water, as well as the chemical constitution of the latter. The results obtained in this study showed that for both dyes studied, analyzed at 50 mg/L, the color disappears after 30 min of ozonation.

Figure 6 shows the discoloration for the studied dyes at 50 ppm. Based on the preliminary analysis, it can be stated that the discoloration of the RR141 and RB160 is almost identical.

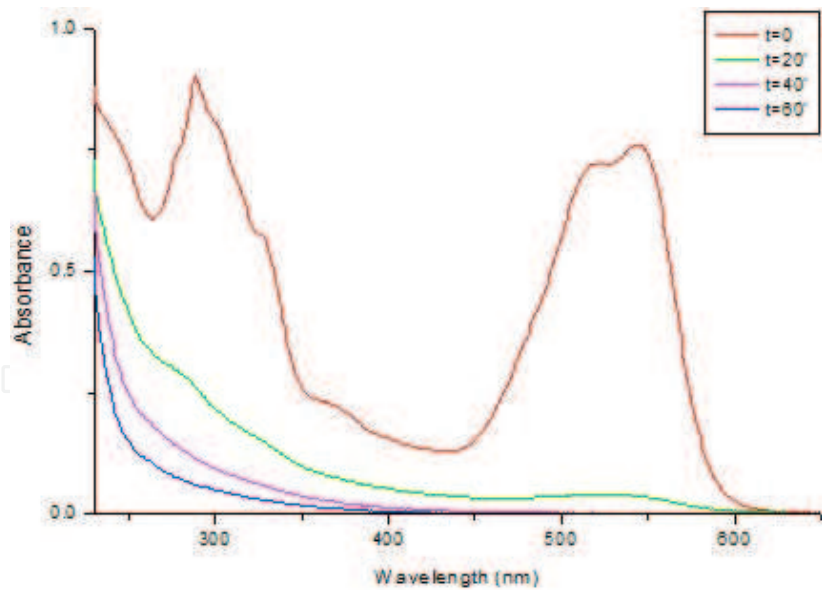


Figure 4.
Variation of the UV-Vis spectrum of RR141 during ozonation.

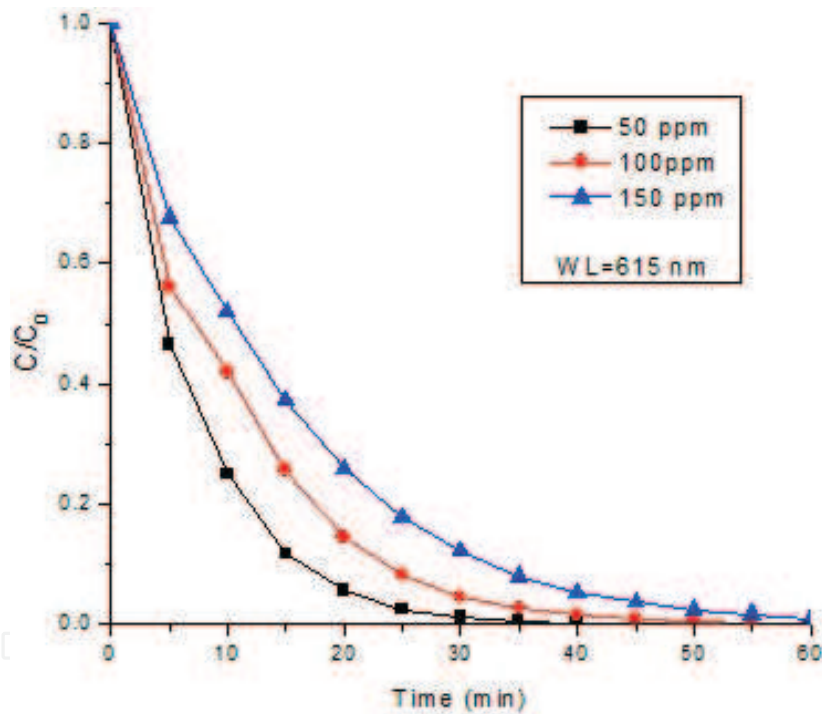


Figure 5.
Influence of concentration on discoloration of RB160 during ozonation.

RR141 has four amino groups and seven sulfonic groups, while RB160 has five amino groups and five sulfonic groups. Thus, taking into account the proportion between sulfonic groups and amino groups in the dye molecules, their reactivity and molecular weight, the observed discoloration rates are consistent. **Figure 7** shows the degradation of the dyes studied, during 60 min of ozonation and with an initial concentration of 50 mg/L.

The by-products of the two dyes require for their destruction of ozonation times greater than the 30 min necessary for the discoloration. Both curves are almost identical.

These results agree with the conclusions obtained by other researchers, who associate the presence of amino groups in the molecules of the dyes to a very fast reaction with ozone, while the presence of sulfonic groups increases the resistance

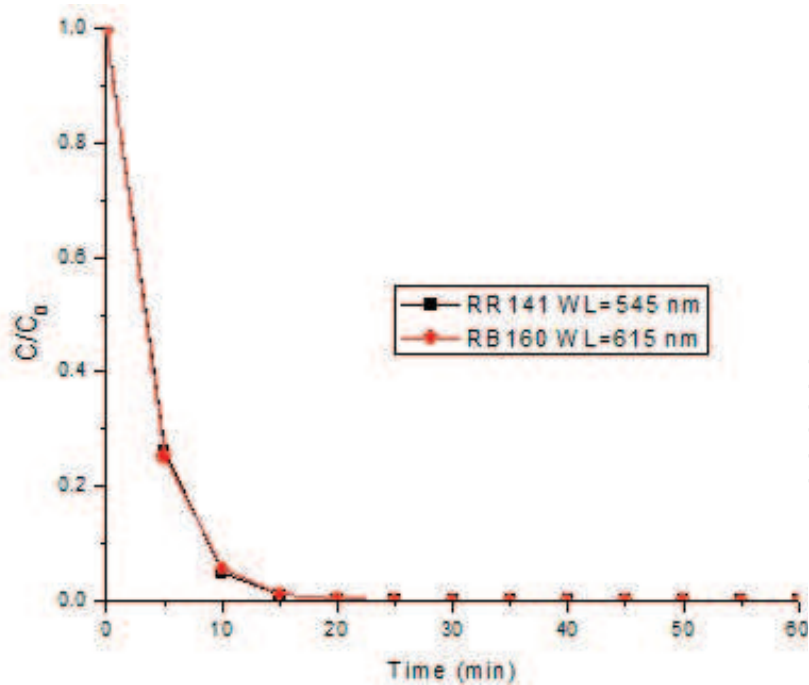


Figure 6.
Discoloration of the compounds studied at 50 mg/L.

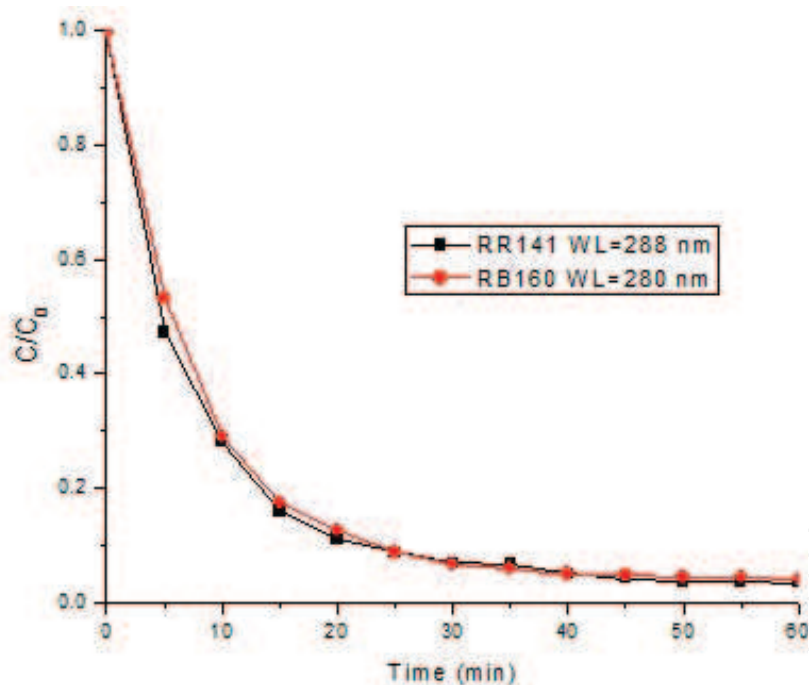


Figure 7.
Degradation of the dyes studied at 50 mg/L.

of the dye toward the attack with ozone [7, 11]. The composition of the intermediates and final ozonation products depends on the chemical structures of the dyes. Phenols, quinones, hydroquinones, and acids such as phthalic, muconic, fumaric, maleic, etc. have been identified among ozone intermediates. The final products that have been identified are sulfate and nitrate ions, elemental nitrogen, and oxalic and formic acids [11, 12].

If one takes as a starting point the mechanisms proposed in the literature for the degradation of organic compounds, the formation of maleic acid precedes the formation of oxalic acid and is carried out from the first minutes of ozonation.

Figure 8 shows the variation of the pH during ozonation of the dyes [7].

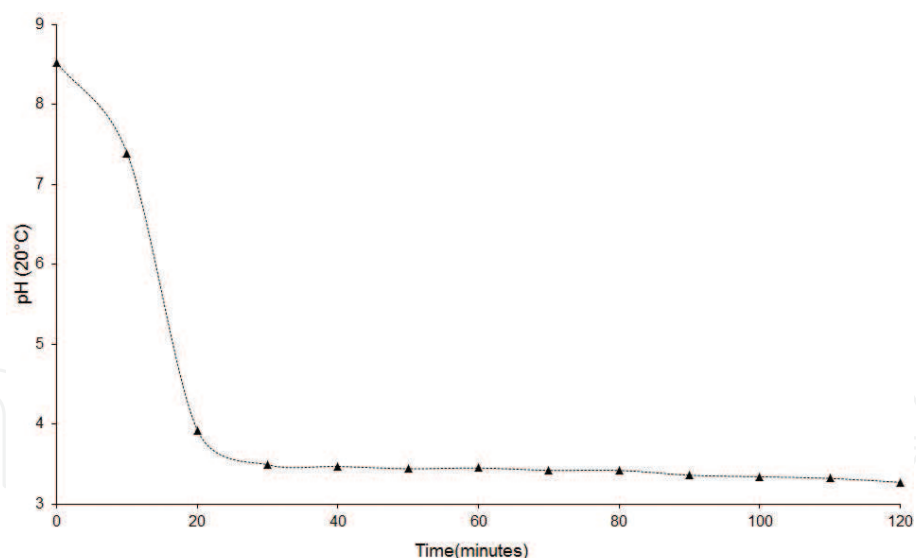


Figure 8.
pH variation during ozonation for RR141 at 50 mg/L.

The decrease of the pH in the ozonation of the dyes contributes to verify, in an indirect way, the formation of organic acids during the ozonation process. It is known that during the first minutes of ozonation, the formation of maleic acid is observed, the concentration of which then decreases markedly. However, the pH continues to decrease due to the subsequent formation of oxalic acid, which continues to form and accumulate throughout the ozonation process, although at a slower rate. It has been found that ozonation induces the denaturation and desulfurization of sulfo- and nitrophenols in the first stage of the reaction [13]. The increase in the conductivity of the dye solutions in ozonation serves as an indirect confirmation of the formation and accumulation of sulfate and nitrate ions, which in turn confirm the denitration and desulphurization of the dyes in the first step of the reaction. **Figure 9** shows the variation of conductivity for RR141 during ozonation [7].

During the process of dyeing textile materials with reactive dyes, the addition of large amounts of salt is necessary to promote the incorporation of the dye into the fiber. **Figure 10** shows the effect of salt addition on the ozonation of RR141 at 50 mg/L.

Once the dye is inside the fiber, it is necessary to add alkali, in order to promote the formation of the covalent bonds characteristic of this class of compounds. **Figure 11** shows the effect of adding sodium carbonate during ozonation for RR141 and **Figure 12** shows the effect of sodium hydroxide.

Due to this, the effluents of the dyeing with reactive dyes present considerable quantities of both salts and alkalis [7]. To study the influence of these inorganic substances, solutions of 50 mg/L of each of the dyes were prepared, and variable amounts of Na_2SO_4 , Na_2CO_3 , and NaOH were added to them before they were subjected to ozonation. The presence of inorganic auxiliaries in the dye solution has influence on the kinetics of discoloration. However, the concentration of these salts has no important influence on the kinetics. As an example, for RR141 and first-order reaction, rate constant is 0.0264 min^{-1} without addition of sodium sulfate, 0.0299 min^{-1} with addition of 10 g/L of salt, and 0.0303 min^{-1} with 20 g/L.

During the process of partial oxidation of the dyes with ozone, intermediate products are formed. These products accumulate through the recirculation cycles of the treated water and can influence the quality of the dyes made. **Figure 13** shows the accumulation of partial oxidation products through the consecutive recirculations for RR141.

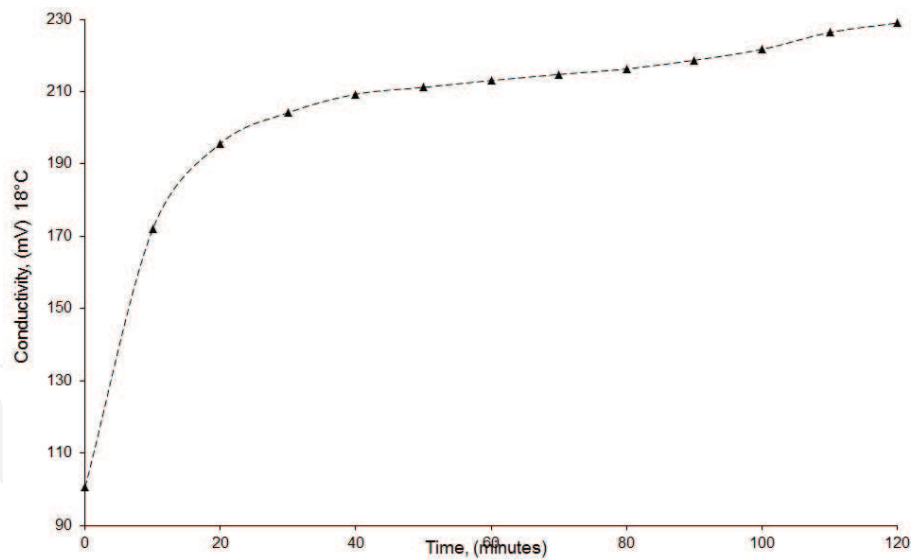


Figure 9.
Conductivity variation during ozonation for RR141 at 50 mg/L.

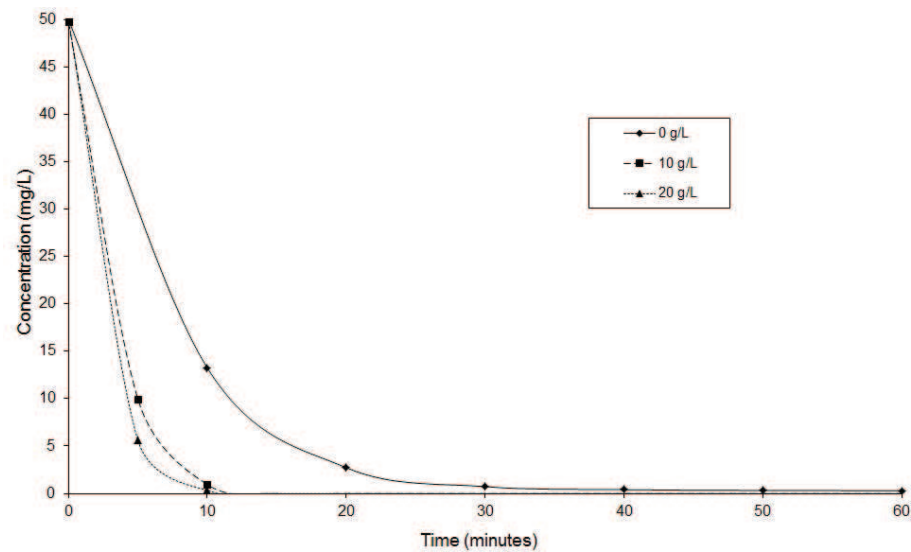


Figure 10.
Effect of salt addition during ozonation for RR141.

The water recycled up to five times by the procedure described in the methodology was used to make dyes on cotton cloth with direct dyes (AD80, AD50, and RD23) and with reactive dyes (AR84, RR141, and NR5). The determination of the quality of the coloration of these dyes was carried out by means of the AATCC method Test Method 173-2005 Calculation of Small Color Differences for Acceptability [9]. **Figure 14** illustrates the behavior of dyes made with direct dyes and reagents, in terms of the color difference coefficient (ΔE), when using RR141 solutions treated with ozone with up to five recirculation cycles of the pretreated water. A value of ΔE less than one means that the quality of the dye is acceptable.

Figure 14 shows that water contaminated with RR141 and pretreated can be used for dyeing processes with direct dyes during four cycles tested without significantly affecting the quality of the dye. The dye that best behaves in this case is Direct Blue 80 (AD80), which belongs to group B of the SDC classification, while Direct Yellow 50 (AD50) and Direct Red 23 (RD23), belonging to groups A and C, respectively, are very similar in their behavior. Regarding the reactive dyes, it is observed that it can be dyed with them without the coloration being affected for

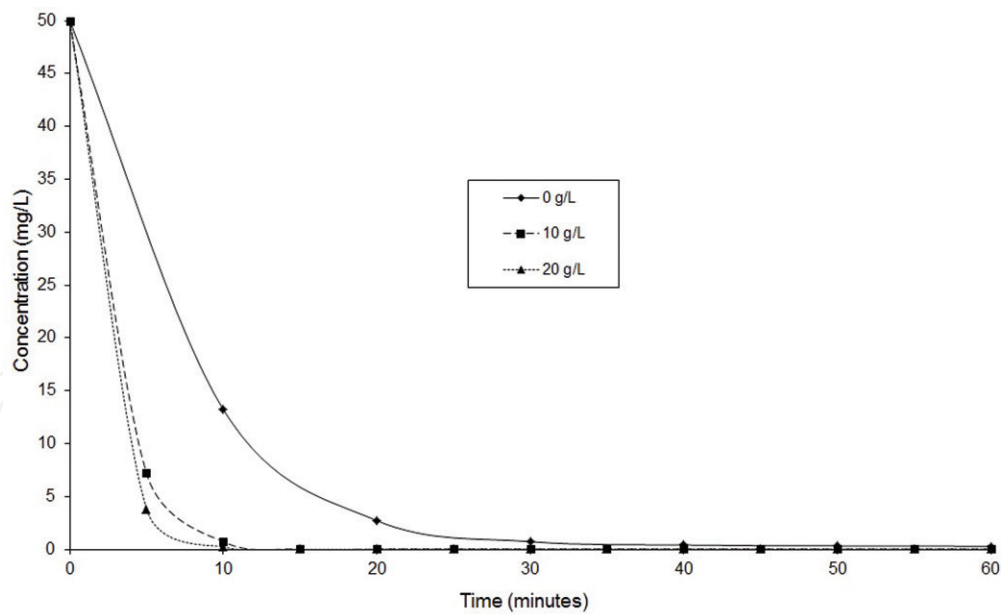


Figure 11.
Effect of sodium carbonate addition during ozonation for RR141.

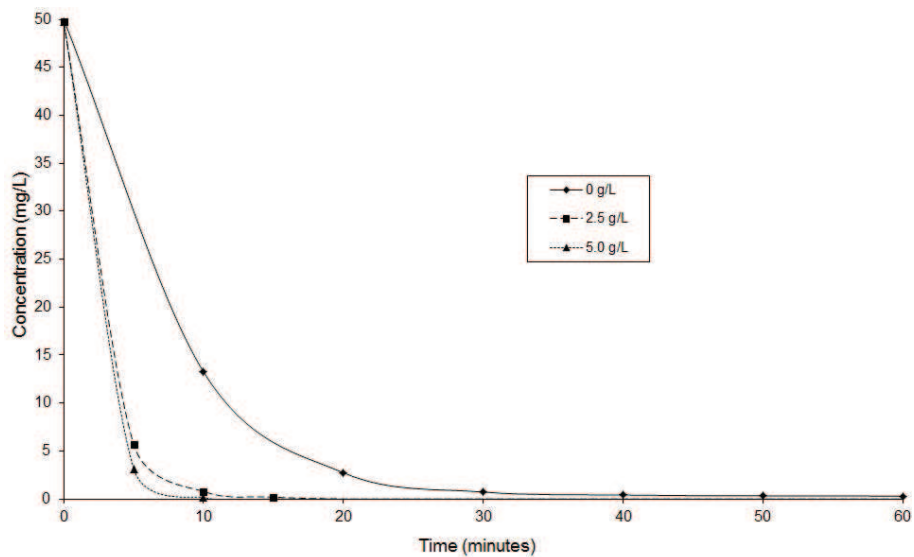


Figure 12.
Effect of sodium hydroxide addition during ozonation for RR141.

up to four cycles. Even though the NR5 presents differences of $\Delta E > 1.0$ from the second cycle, the results can be considered acceptable, since this dye is generally used at concentrations above 5% of the weight of the textile material, which makes it possible to hide the differences of coloration.

During the dyeing processes with reactive dyes, important quantities of sodium salts, mainly sodium sulfate, are added. The function of this salt is to neutralize the negative charge that the fiber acquires when impregnated with water. This function is performed by the sodium ion [11]. To verify that the sodium ion is not affected by the ozonation process, solutions were prepared as in the case of dye recirculations, with initial concentrations of 50 mg/L, both dye and sodium. The sodium ion content was analyzed by atomic absorption spectroscopy at 303.2 nm. **Figure 15** illustrates the result of the analysis for RR141 [14].

It can be observed that the content of sodium ion does not decrease during ozonation, which is the condition for the process to have an economic attraction

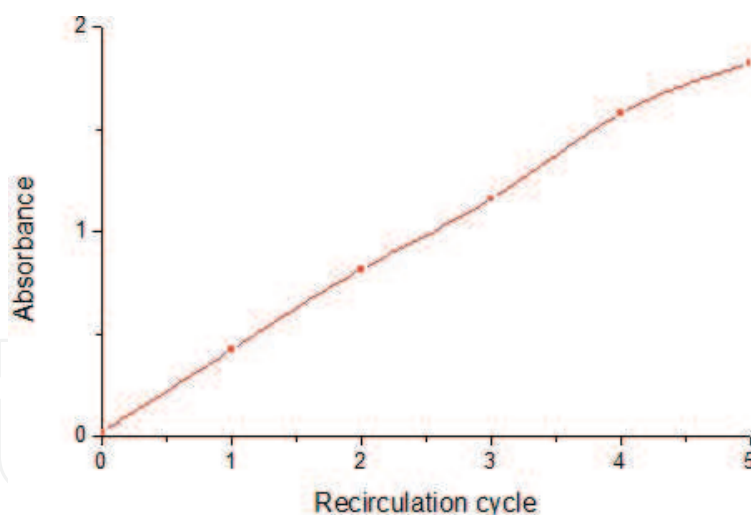


Figure 13.
Accumulation of products in the ozonation of RR141 with water recirculation.

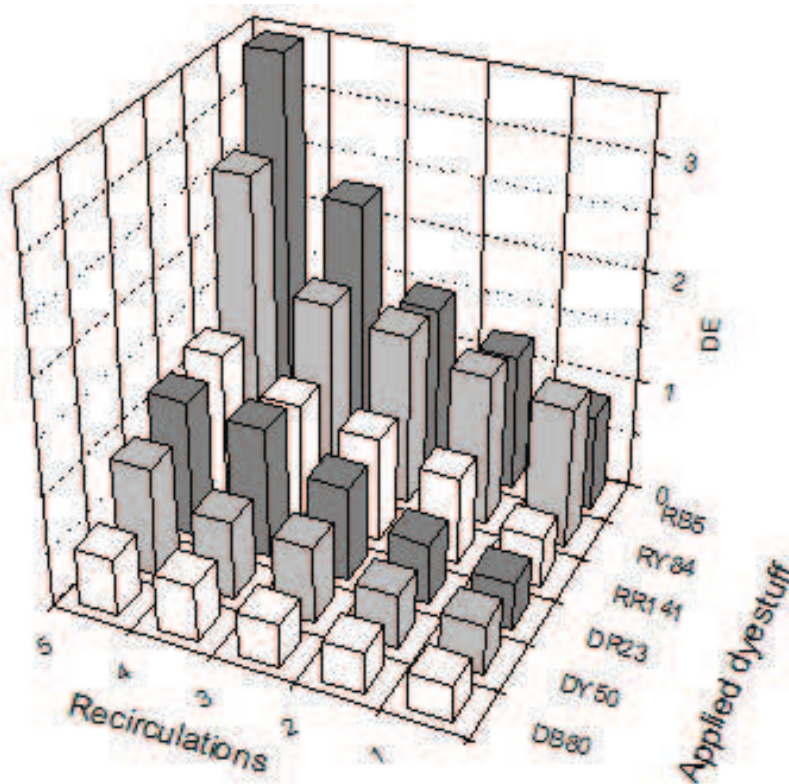


Figure 14.
Color differences obtained by dyeing cotton by reusing ozonated RR141 solutions.

due to the recovery of the salt contained in the exhausted dyeing bath. In fact, the sodium ion content increases slightly, due to the presence of ions of this type in the structure of the dyes and in the salts used in their manufacture to standardize them at commercial concentration.

A preliminary analysis by FTIR of the changes in the structures of the dyes during ozonation was carried out. In the area between 2000 and 4000 cm^{-1} , appears only one band at 3450 cm^{-1} ; which corresponds to stretches of phenols or aromatic amines. **Figure 16** shows that region for RR141.

In the region between 600 and 2000 cm^{-1} , the dyes have several common absorption bands. One of them at 620 cm^{-1} , of bending of SO_3^- , together with another one at 1140 cm^{-1} , of stretching of bond $\text{S}-\text{O}$, confirms the desulfonation

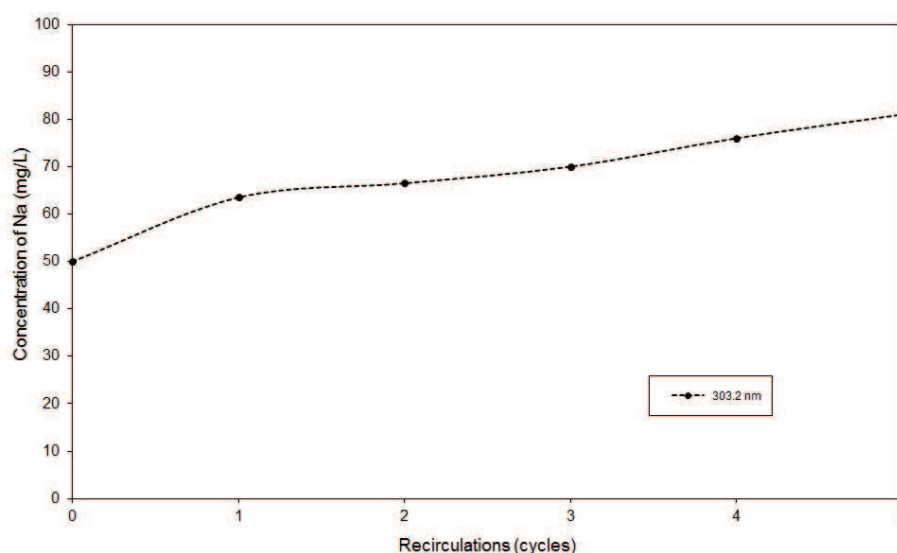


Figure 15.

Analysis by means of atomic absorption of the presence of sodium ion during the recirculation of water contaminated with RR141.

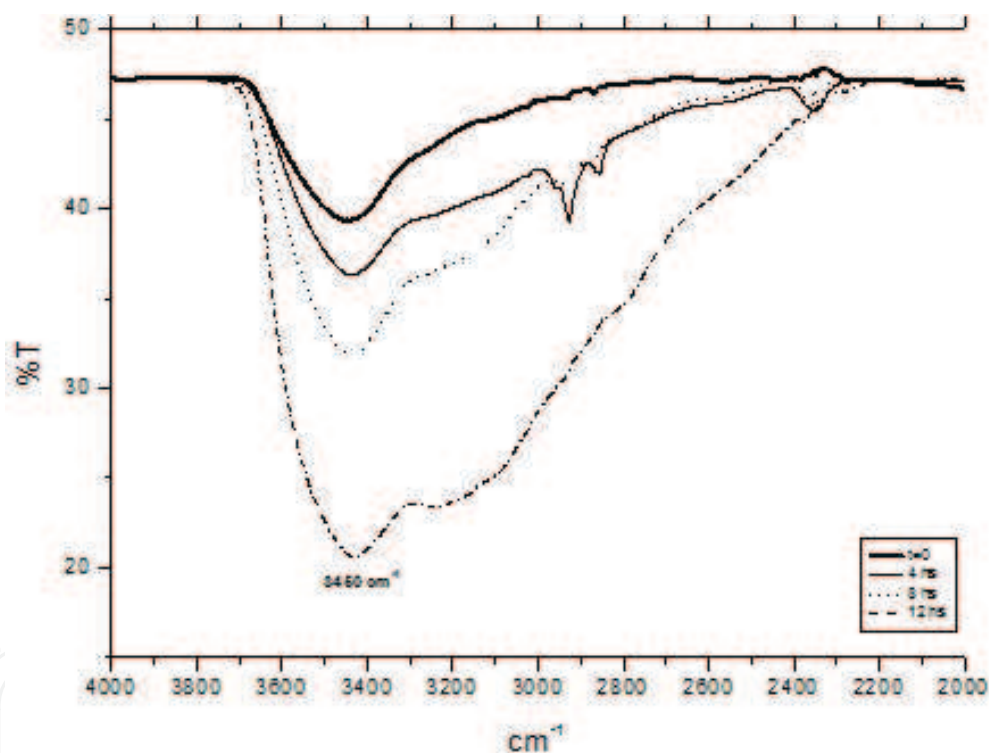


Figure 16.

Variation of the FTIR spectrum of RR141 during ozonation, between 2000 and 4000 cm^{-1} .

of the compounds during ozonation. Also, a band at 1050 cm^{-1} , of stretching of C—O bond, and a band located at 1400 cm^{-1} , of COO— ion stretching, confirm the formation of organic acids. Additionally, the dyes have absorption at 1500 cm^{-1} , corresponding to NO_2 formation, and at 1620 cm^{-1} , which indicates the formation of secondary amines.

RR141 show absorption at 760 and 1720 cm^{-1} . The first one corresponds to vibrations of the aromatic ring, while that of 1720 corresponds to the vibration of the -COOH group and indicates the formation of carboxylic acids. **Figure 17** shows region between 600 and 2000 cm^{-1} for RR141 [15].

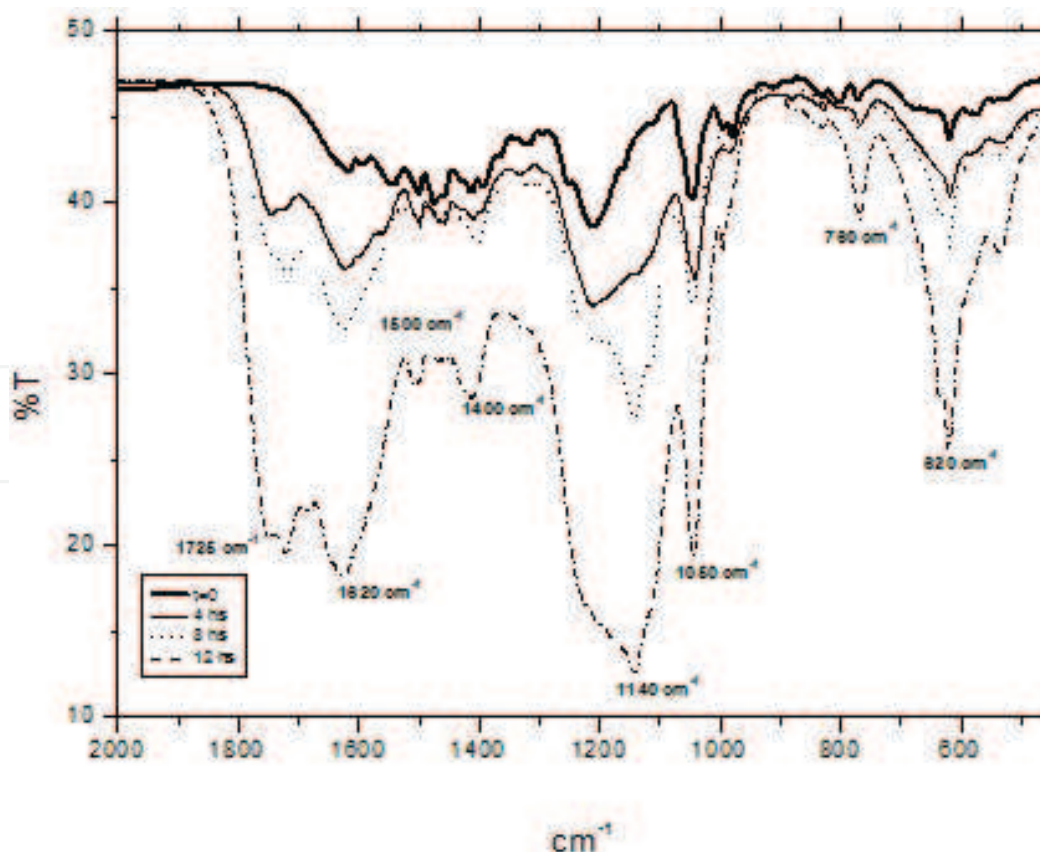


Figure 17.
 Variation of the FTIR spectrum of RR141 during ozonation, between 600 and 2000 cm^{-1} .

4. Conclusions

According to the results, we can conclude the following:

1. The discoloration of the model solutions of RB160 and RR141 dyes by ozonation is carried out during the first 30 min of treatment.
2. The rate of the ozonation reaction for the dyes is different and depends mainly on the chemical structure of the dye used, the initial concentration of this, and other factors, such as the dyeing auxiliaries.
3. In addition to the discoloration, it is possible to decompose the intermediates present in the water, until obtaining biodegradable and nontoxic compounds such as organic acids, if the ozonation time is prolonged.
4. During the cycles of recirculation of the water, an accumulation of ozonation products is observed. However, these products allow water to be reused for several cycles, depending on the type of dyes used in dyeing with treated water. In addition, such ozonation products can be degraded by longer ozonation times (>120 min).
5. A water recirculation scheme was proposed in dyeing processes of textile materials, both with reactive dyes and with direct dyes, which does not affect the quality of the dyeing result.

6. It was shown that the proposed recirculation scheme works properly using water that has been premixed for a period of 10 min, up to four cycles, for the case of dyeing with direct dyes, and up to four cycles, for the case of dyeing with reactive dyes.
7. Likewise, it was demonstrated that the sodium ion content is not affected by ozonation during the water recirculation cycles. In fact, it increases slightly, due to the sodium ions contained in each dye, both in its molecular structures and in the salts used to standardize them.
8. Some of the advantages of the reuse of water treated by ozonation according to the proposed scheme are the following:
 - Elimination of a good part of the color in the discharges into the environment, decreasing visual pollution.
 - Elimination of the use of other treatments, such as the addition of polymers, or the use of membranes that are effective, but at the same time costly, and do not eliminate the problem.
 - Improvements in the final treatment of wastewater, because the decomposition products of the dyes are more biodegradable than the dyes themselves.
 - Reduction of the consumption of water and salts used in the dyeing, as well as reduction of discharges of salts to the environment. These salts are sulfate and sodium chloride, mainly, and are used during the dyeing to facilitate the diffusion of the dye in the textile material.
 - The recovery of the salts and water used, by itself, makes economically attractive the reuse of spent dyeing baths, especially in the case of reactive dyes, where the salt concentration in the dyeing bath becomes approximately 10% w/v.

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Conflict of interest

The author declares that he has not conflict of interest.

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