

Treatment of Textile Industrial Dyes by Simple Ozonation with Water Recirculation

Tatyana Poznyak,¹ Pablo Colindres¹ and Isaac Chairez²

¹ Escuela Superior de Ingeniería Química e Industrias Extractivas, Instituto Politécnico Nacional, Edificio 7, UPALM, Zacatenco C.P. 07738, México, D.F. E-mail: tpoznyak@mail.ru, tpoznyak@ipn.mx

² Departamento de Control Automático, CINVESTAV-Instituto Politécnico Nacional, Av. Instituto Politécnico Nacional, Col. San Pedro Zacatenco, C.P. 07360, México D.F., jchairez@ctrl.cinvestav.mx

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Abstract. In this study, three textile dyes are destroyed by ozone in water solution. These dyes were selected because of their complex chemical structure and extended application in textile industry. Decomposition of dyes by simple ozonation was observed at the initial pH of the aqueous colorants solutions UV-VIS analysis was used for preliminary control of the degree of decomposition. HPLC analysis was used to identify intermediates and final products formed during ozonation. It was shown that color disappears completely for all dyes after 1.5 - 2 min of ozonation. The pre-ozonated water was used for the preparation of colorant solutions until 8 times. The dyeing quality (using pretreated solutions) was determined by the standard AATCC method. In the water pre-ozonation byproducts accumulation was observed, but their presence in the solution did not affect the color quality. The ozonation of dyes solutions has not any influence on the coloration quality in 6 times water recirculation for DR28 and BG4, and in 8 times water recirculation for RB5. After several times of water recirculation ozonation procedure was conducted during 20 min to destroy intermediates. Dyes are completely destroyed in ozonation with the formation of final products (malonic and oxalic acids).

Keywords: Dyes decomposition, simple ozonation, water recirculation.

Resumen. En este estudio, tres soluciones acuosas diferentes de colorantes textiles son tratadas con ozono. La selección de los colorantes fue realizada debido a su estructura química y a su aplicación en la industria textil. La descomposición de los colorantes por ozonación simple fue observada en las soluciones en agua correspondientes El análisis UV-VIS fue el método preliminar para controlar el grado de descomposición del colorante. Se empleó HPLC para identificar los intermediarios y los productos finales formados durante la ozonación. Se observó la desaparición del color para todos los colorantes después de 1.5-2 min de ozonación. El agua ozonada fue utilizada para la preparación de colorantes hasta en 8 ocasiones. La calidad del proceso de tintura a partir de la solución pre-tratada fue determinada por el método estándar AATCC. La presencia de algunos subproductos de rápida formación se observó en las muestras, sin embargo, esta no afectó la calidad final del agua. El tiempo reducido de ozonación sobre los colorantes no tiene influencia en el proceso de coloración del RD28 y del VB4 hasta en 6 recirculaciones, mientras que en el caso del NR5 el proceso se pudo repetir hasta en 8 ocasiones. La etapa final del tratamiento por ozonación consistió en la realización de una reacción entre la mezcla, obtenida después de las recirculaciones y ozono durante 20 min. Los colorantes fueron totalmente eliminados y se presentó la acumulación de dos productos finales de baja toxicidad (ácido oxálico y malónico).

Palabras Clave: Descomposición de colorantes, ozonación simple, recirculación de agua ozonada.

Introduction

Textile industries consume large amounts of water and their effluents contain a wide range of contaminants. These contaminants are dyes with strong color, inorganic salts, as well as high pH. Textile wastewater containing significant concentration of dyes cause substantial treatment problems. Most of the dye molecules have a polyaromatic structure with high molecular weight and contain atoms of nitrogen, sulfur and metals; hence it is very difficult to break them down by any biological method and they cannot be treated efficiently by an activated sludge or some combination of biological, chemical or physical methods [1]. The ozone usage in the textile water treatment is expanding as water quality requirement [2, 3]. Ozone destroys the conjugated chains of the dye molecules to impart color [4-8]. The decoloration of azo-dyes is fast and thus, the kinetic constants for a second order reaction obtained by different methods are 10^5 - 10^7 L/mol s [9, 10]. The industrial textile wastewater is a complex multi-component mixture and consists of some compounds similar to anthraquinone dyestuff,

anionic detergents, softening agents and some inorganic salts like sodium chloride (NaCl).

The combination of advanced oxidation processes (AOPs) with the biodegradation is a suitable alternative treatment for the industrial textile wastewater [11] that permits to obtain 90% of the chemical oxygen demand (COD) reduction. In this particular case, the inhibition effect of the AOPs on microbial growth account is about 10%, while untreated wastewater exhibits 47% of inhibition. Ozone affects the colorants by direct reaction (with ortho- and para-directing substitute -OH, -CH₃, -OCH₃) and by indirect reaction with OH-radicals. In view of the results obtained by Maciejewska [12], it may be concluded that the rate of the dyes decoloration in acidic solution is independent of the ozone decomposition provided by basic pH condition. In the textile dyes case, just the direct ozonation mechanism takes place.

In this study, three textile dyes (reactive black 5 (RB5), direct red 28 (DR28) and basic green 4 (BG4)) are treated by simple ozonation. The ozonation at the initial pH of the aqueous colorants solutions (6.5 for RB5, 6.9 for

DR28 and 3.7 for BG4) was carried out. These dyes were selected because their complex chemical structure and in view of their extended application in the textile industry. Table 1 presents the real concentration of colorants in residual water. The summary information of the organic pollutants decomposition dynamics was followed by UV-VIS absorbency variation (190-700 nm). The decolorization dynamics by the same technique was also analyzed. To study the effect of the water pre-ozonation on in the water recirculation, the colorants solution is prepared 8 times. The dyeing quality was determined by the standard AATCC method (Calculation of Small Color Differences for Acceptability) Test Method 173-1998 applied in the textile industry (AATCC, 2000) is used [13].

Experimental

In this study, a synthetic textile wastewater was prepared in order to simulate the effluent from a dye house. The studied textile dyes were reactive black 5 (RB5), direct red 28 (DR28) and basic green 4 (BG4) with the concentrations of 50 and 150 mg/L. All studied chemicals are industrial samples. In Figure 1 the chemical structures of dyes are presented.

Ozonation Procedure

The ozonation of the dye solutions is conducted in a semi-batch reactor (500 mL) with the initial ozone concentration of 24-31 mg/L. The ozone-oxygen mixture flow is fixed at 0.5-L min⁻¹. All experiments were carried out at 20°C with agitation by bubbling of the recently mentioned ozone-oxygen mixture. The reactor system includes a by-pass for the gas mixture. This particular reactor construction allows controlling the gas flow into or out of the reactor. The ozonation experiments have been developed with the initial neutral pH (6.5 and 6.9) for RB5 and DR28, and at the initial acidic pH (3.7) for BG4 (this are the initial dyes solution pHs).

For all experiments, 3-mL aliquots of the reaction solution were withdrawn at desired time intervals from the reactor for sequent analysis. Figure 2 represents the schematic diagram of the ozonation apparatus.

Ozone was generated from dry oxygen by an ozone generator (corona discharge type) HTU500G ("AZCO" Industries Limited-Canada). An Ozone Analyzer BMT 963 (BMT Messtechnik, Berlin) provides the ozone detection in the gas phase at the reactor outlet. These measurements were used for the ozone monitoring, the control of the ozonation degree, the ozone consumed and the ozone decomposition.

Analytical methods

The preliminary information on the colorants decomposition dynamics was obtained by UV-VIS absorbency at 190 – 700 nm. The analysis was carried out by a spectrophotometer Perkin Elmer-Lambda 2B. The dyes decoloration dynamics

Table 1. Dyes concentration in residual water.

Dye	Concentration, mg/L
RB5	90 - 225
DR28	12.5 - 75.0
BG4	5.0 - 12.5

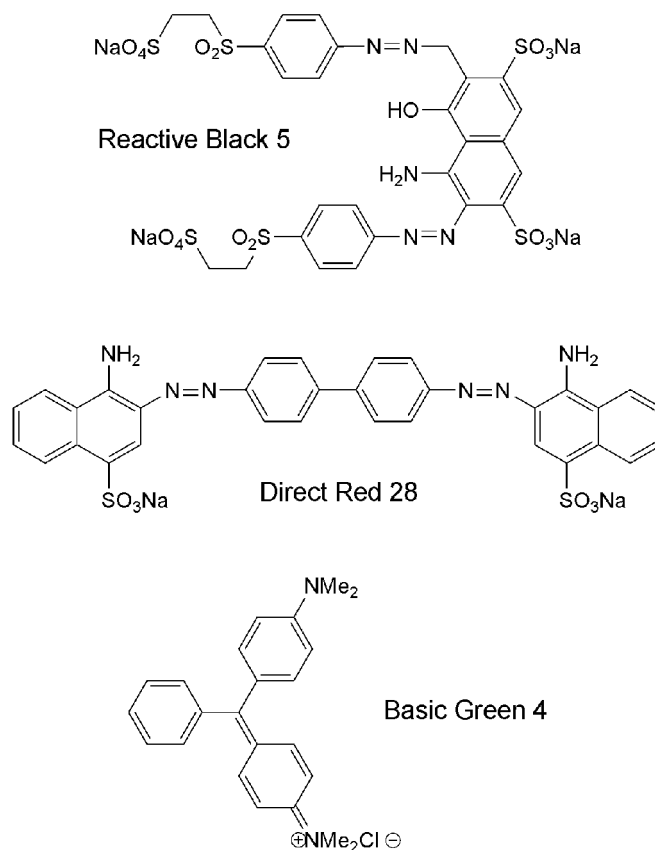


Fig. 1. Chemical structure of the studied dyes.

was obtained by UV-VIS spectrum variation at 497.5 nm for DR28, at 582 nm for RB5 and at 425 nm for BG4.

The control of the dyes decomposition as well as the intermediates and final products identification has been achieved by a high performance liquid chromatography (HPLC) analysis, (Perkin Elmer) equipped with UV-VIS detector series 200 (190-460 nm). A reverse phase column was of Spheri-5 ODS 5 μ k, 250 mm in length and 4.6 mm in diameter. The used mobile phase was selected water: acetonitrile: phosphoric acid 95.0:4.8:0.2 for dyes, 50.0:49.9:0.1 for phenol derivates and 89.9:10.0:0.1 for acids expressed as volume ratio with a flow rate of 0.8 mL min⁻¹. The colorant dynamics decomposition, the retention time and the UV spectrum patterns at different wavelengths was used (see Table 2).

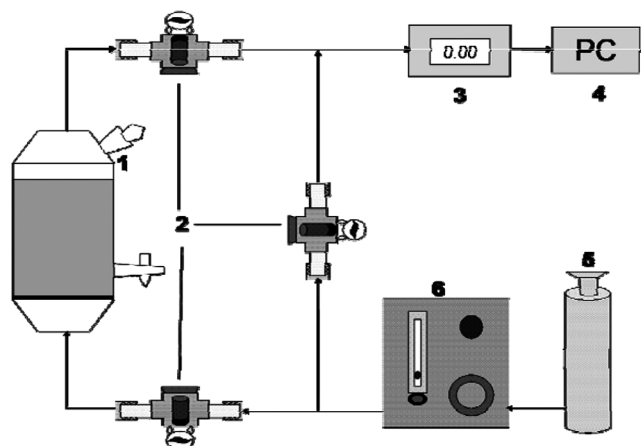


Fig. 2. Schematic diagram of the ozonation apparatus: reactor (1), bypass – system (2), ozone analyzer (3), PC (4), ozone tank (5) and ozone generator (6).

Table 2. Retention times of compounds used in the HPLC analysis.

Compound	Retention time, min
Hydroquinone	3.18
Catechol	3.70
Phenol	4.87
The mobile phase	H ₂ O: ACN: H ₃ PO ₄ 50: 50: 0.1
Oxalic acid	2.68
Maleic acid (Malonic acid)	3.87
The mobile phase	H ₂ O: ACN: H ₃ PO ₄ 89.9: 10: 0.1
RB5	2.76 ($\lambda = 311$ nm)
DR28	2.81 ($\lambda = 343$ nm)
BG4	3.22 ($\lambda = 210$ nm)
The mobile phase	H ₂ O: ACN: H ₃ PO ₄ 95: 4.8: 0.2

Results and Discussion

Color Removal and the Dyes Destruction

According to bibliographic records [14], the first stage of decoloration for many dyes involves, probably, the reaction of ozone with a single chromophoric group such as an azo group or a carbon-carbon double bound connecting aromatic rings. Maciejewska [12] concludes that in acidic solution the dyes ozonation is carried out by the direct mechanism. The results obtained in the present study show that color disappears completely for all dyes after 2 min of ozonation. Figure 3 presents

the UV-VIS spectrum variation for RB5 during 5 min of ozonation. As one can see from these spectrums, the dye is destroyed by ozone very rapidly after 1.0-1.5 minutes. A similar tendency is observed for the three dyes as can be observed in Figure 4, which presents the decoloration dynamics.

The dyes are destroyed by ozone with the by-products formation. Figure 5 presents the concentration variation of the ozonation by-products summary. It may be concluded that the intermediates from the three colorants are decomposed after the ozonation time of 7 to 20 min. As one can see from Figure 6, the time of the dyes decomposition is quiet different. Indeed, RB5 is decomposed in 10 minutes, while the DR28 is completely eliminated before 1 minute. These results coincide with those obtained by other researches [14, 15], as well as the presence of amino groups in the dye molecule, which is associated with a faster ozone reaction. Additionally, the presence of sulfonic groups is associated with the resistance increasing of the dye to the ozone attack.

According to bibliographic data [14, 16], the intermediates and final products of the dyes ozonation reaction depend on their chemical structure. So, among the intermediates, phenols, quinones, hydroquinones, phtalic, muconic, fumaric, maleic acids, etc. one can identify. However, all of these by-products were identified at short ozonation times and disappear completely at reaction times bigger than 15 minutes. On the other hand, sulfate ions, nitrate ions, elemental nitrogen, oxalic and formic acids were identified as final accumulated products.

In the present study, the intermediates from ozonation are completely destroyed after 25 min with the final formation of oxalic acid. This compound is classified as the final reaction product. In the RB5 and BG4 ozonation malonic acid formation is observed too. A corresponding decrease of the pH value in ozonation was used as an indirect confirmation test of the organic acids formation in the dyes decomposition (Table 3). In the case of the BG4 decomposition, the pH does not vary in ozonation. The Figure 7 presents the pH variation during dyes ozonation. As can be seen, the pH decreases to minimal values after few seconds of ozonation and it does not vary after 5 minutes.

It was found [17-20] that ozonation induces the denitration and desulfuration of phenols as the initial reaction stage. In the present study, the increase of the dyes solution conductivity may serve as an indirect confirmation of sulfate ions and nitrate ions accumulation, and in turn, it confirms the denitration and the desulfuration of dyes in the initial steps of ozonation. Figure 8 represents the conductivity variation of the dyes solutions in ozonation. As one can see from these data, the conductivity dynamics for RB5 and DR28 is practically same, while the BG4 conductivity dynamics is slower. This depends on the chemical structure of organics and on the stoichiometry of the reaction each dye with ozone.

Effect of the Pre-Ozonation on the Water Recirculation Times

The pre-ozonated water was used for the colorant solution preparation 8 times, and was examined by the dyeing quality

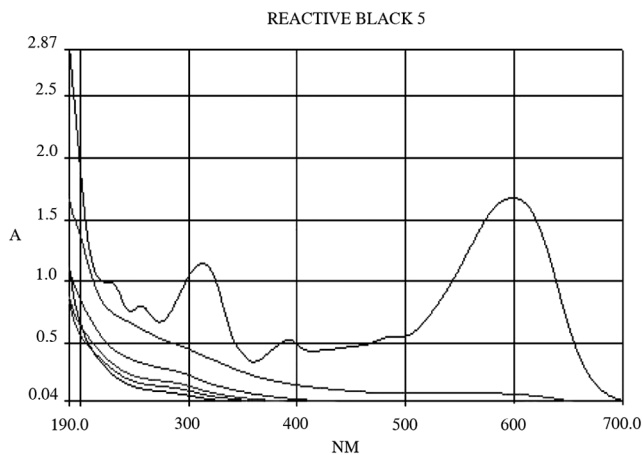


Fig. 3. The RB5 spectrum variation during ozonation (5 min).

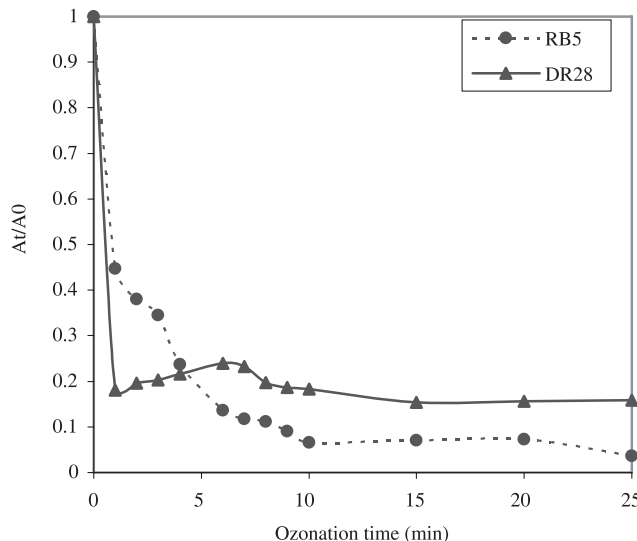


Fig. 6. Decomposition dynamics of RB5 and DR28.

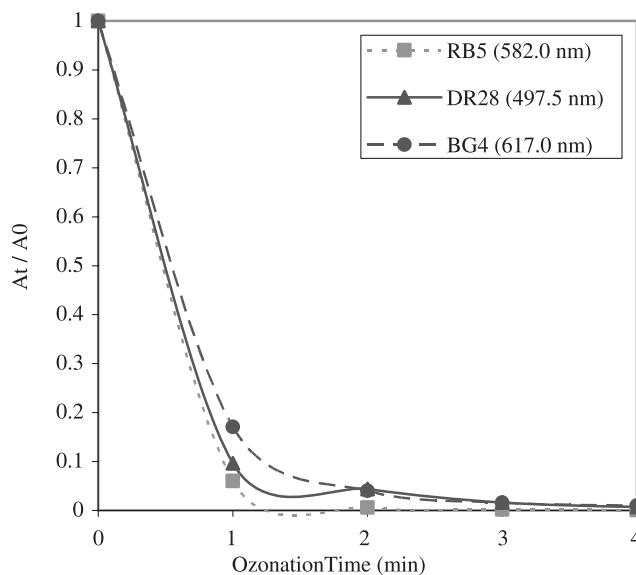


Fig. 4. Dyes decoloration dynamics of RB5, DR28 and BG4 in ozonation.

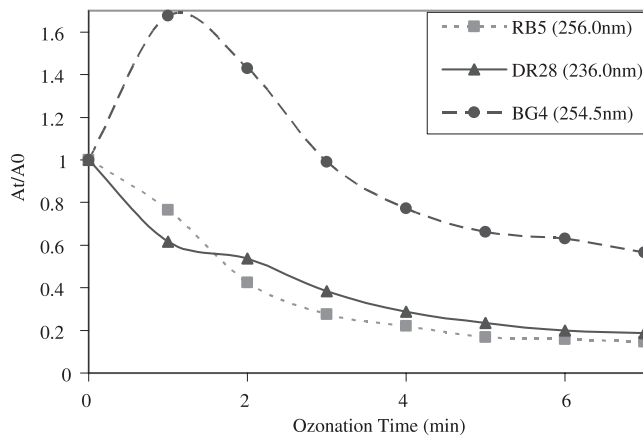


Fig. 5. Variation of the ozonation by-products for RB5, DR28 and BG4.

Table 3. pH variation of solution in ozonation.

Dye	Initial pH	Final pH
RB5	5.0	2.5
DR28	7.5	2.5
BG4	2.5	2.5

determination using the standard AATCC method. The corresponding tests provide information about the number of times that the ozonated water can be reused. Table 4 presents the experimental data of the color coefficient variation (AE) for studied dyes in the water recirculation. In view of these data, the short water ozonation during 1.0 - 1.5 min has no influence on the coloration quality. The short ozonation of the dyes does not have influence on the coloration quality in 6 water recirculation for DR28 and BG4, and in 8 water recirculation for RB5. In the initial stages of ozonation it is observed the by-products accumulation in water (Fig. 10), but the presence of these compounds does not have any influence on the reused water quality. After *i*-times water recirculation (6 times for RB5 and BG4; 8 times for DR28) the ozonation procedure is conducted more prolonged time of 20 min for the final products (malonic and oxalic acids) formation.

Kinetic Study of Dyes Ozonation

Dyes ozonation mechanism is very complex, and its interpretation on the base of the composition of intermediates and final products only is difficult. To obtain more information about reaction mechanism it is necessary to investigate kinetics of ozone reaction with colorants. On the base of preliminary obtained results [20-23], where the kinetic study of the

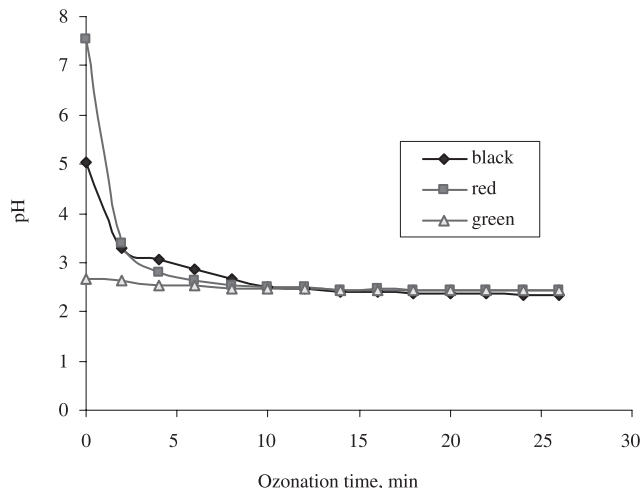


Fig. 7. pH variation in dyes ozonation.

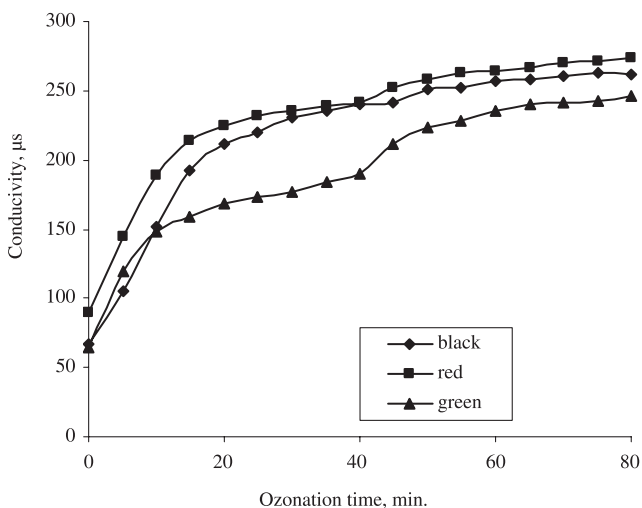


Fig. 8. Conductivity variation of the dyes solution during ozonation.

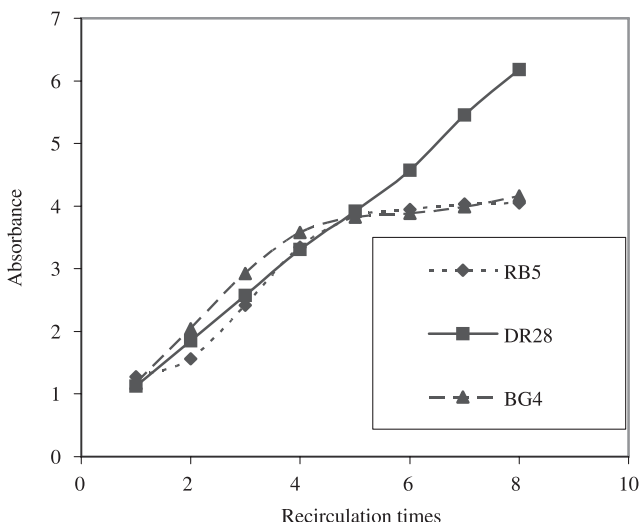


Fig. 9. By-product accumulation in the dyes ozonation throughout the water recirculation.

phenols decomposition dynamics at different pH was carried out, and reaction rate constants were calculated using a simplified mathematical model, the reaction rate constants of ozone with colorants were also calculated using the same model. In order to determine these kinetic constants, the monitoring of ozone concentration in the gas phase at the reactor output was required. Variation of this parameter was used to obtain the characteristic curve of each dye ozonation, which is called ozonogram (Fig. 10 (a) and (b)). This figure shows two different cases: 50 and 150 ppm dye initial concentration. The ozone variation at the reactor’s output is very important to study the dyes dynamics decomposition and the ozonation kinetics.

Using experimental data of dyes decomposition during ozonation reaction obtained by HPLC and UV-VIS techniques (Figures 4 and 6), and applying the suggested mathematical model, the constants of the ozone reaction with dyes molecules in the prime stage of ozonation were calculated. These constants are important variables for the interpretation of ozonation mechanism of colorants in water. At neutral and acidic pH some mathematical models have excellent coincidence with real dynamics of ozonation. Under these experimental conditions, it is possible to estimate the parameter k_i as the solution of the following optimization problem [21]:

$$k_{i,t}^* = \arg \min_{k_i} \int_0^t \left(\frac{d}{d\tau} c_\tau^i + k_i \frac{c_\tau^i Q_\tau}{v^{liq}} \right)^2 d\tau \tag{1}$$

The least mean square method leads to the following solution:

$$k_{i,t}^* = - \frac{v^{liq} \int_0^t c_\tau^i \left(\frac{d}{d\tau} c_\tau^i \right) Q_\tau d\tau}{\int_0^t c_\tau^i Q_\tau d\tau} \tag{2}$$

Decomposition dynamics of the studied colorants corresponds to the high value of the constants obtained by the suggested method. In Table 5, the ozonation constants are presented for two dyes initial concentration of 50 and 150 ppm.

As observed, constant values for three colorants are different and depend on the dyes chemical structure, but they do not change significantly with the initial dyes concentration.

Table 4. Coloration quality coefficient variation (AE) in water recirculation.

Dye	1	2	3	4	5	6	7	8
RB5	0.04	0.58	0.43	0.67	0.50	0.64	0.77	0.84
DR28	0.22	0.45	0.70	0.25	0.86	0.64	1.57	1.13
BG4	0.70	0.76	0.85	0.72	0.88	0.82	1.96	2.02

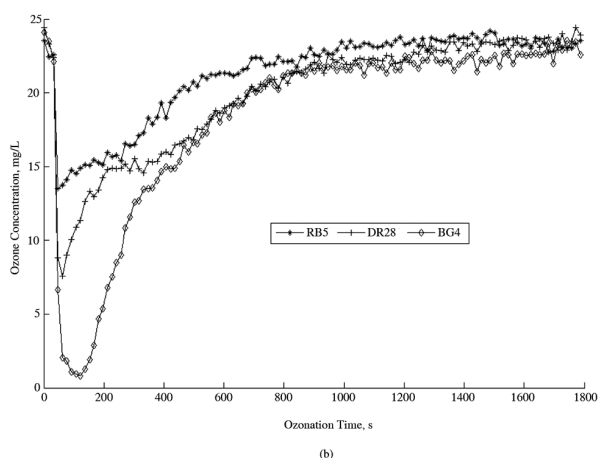
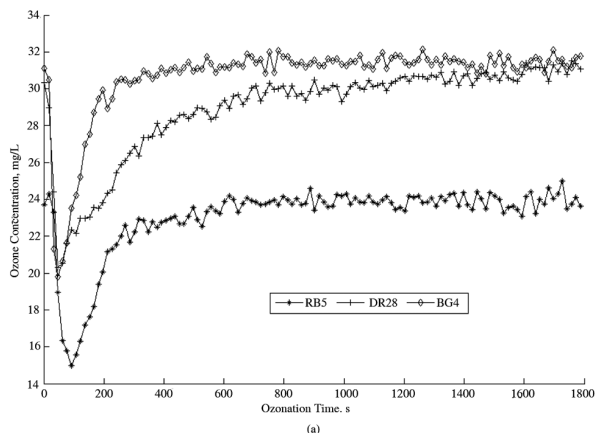


Fig. 10. Ozonographs of three colorants at different initial concentrations: 50 ppm (a) and 150 ppm (b).

Table 5. Constants of dyes ozonation ($L \text{ mole}^{-1} \text{ s}^{-1}$).

Colorant	50 ppm	150 ppm
NR5	5.989×10^4	6.245×10^4
RD28	8.123×10^4	7.989×10^4
VB4	8.656×10^4	8.898×10^4

Conclusions

In view of the results obtained, it may be conclude the following:

1. Ozonation of the dyes studied the complete color elimination after 2 minutes is demonstrated. The dyes decoloration with ozone is simple and fast.
2. The short water pre-ozonation of colorants during 1.5 min has no influence on the coloration quality after 6-8 times water recirculation.
3. The complete decomposition of dyes occurs after 25 min of ozonation.

4. The final products of the dyes ozonation are maleic and oxalic acids.
5. Pretreatment of dye residual water with simple ozonation has been shown to lower the toxicity since all intermediates formed during ozonation are completely decomposed. The ozonation does not generate any toxic chemicals for microorganisms.

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