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# Ozonation of aqueous Bomaplex Red CR-L dye in a semi-batch reactor

Ensar Oguz[a,*], Bülent Keskinler[b], Zeynep Çelik[c]

[a] Atatürk University Environmental Problems Research Center, 25240 Erzurum, Turkey
[b] Gebze Institute of Technology, Environmental Engineering Department, 41400 Çayırova, Kocaeli, Turkey
[c] Atatürk University, Environmental Engineering Department, 25240 Erzurum, Turkey

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## Abstract

The ozonation of synthetic wastewater containing Bomaplex Red CR-L dye has been realized in a semi-batch reactor. In this study, the dye and COD removal from synthetic textile wastewater has been studied by ozonation as functions of initial dye concentration (400, 600, 800 and 1000 mg $L^{-1}$), temperature (18, 40 and 70 °C), ozone–air flow rate (5, 10 and 15 L $min^{-1}$), pH (3, 6, 9.3 and 12) and ozone generation percentage (0.7, 1.1 and 1.4 $O_3$%). The efficiency of dye removal has increased with increasing pH, ozone generation rate, and decreased with increasing temperature, but not changed with increasing ozone–air flow rate and initial dye concentration. The efficiency of COD removal from synthetic wastewater has increased with increasing pH, ozone generation percentage, but scarcely changed with increasing initial dye concentration and ozone–air flow rate, but the efficiency of COD removal decreased with increasing temperature. In this study, dye removal from synthetic wastewater in excess of 99% was obtained at an oxidation time of 15 min. The efficiencies of COD removal were between 56 and 35% at an oxidation time of 30 min. At the end of the study, it was concluded that ozonization is an efficient process for dye removal from synthetic wastewater of Bomaplex Red CR-L, but alone ozonization was not an efficient method to remove all the COD from the textile wastewater.

*Keywords:* Ozonation; Dye; Oxidation; Wastewater; COD

## 1. Introduction

The oxidation potential of ozone (2.07 V) is 1.52 times higher than that of chlorine. The high oxidation potential allows it to degrade most organic compounds [7]. The oxidizing ability of ozone is derived from the third, or nascent, oxygen atom [1]. Ozone and hydroxyl radicals ($OH^{\cdot}$) generated in the aqueous solution are able to open the aromatic rings.

The use of ozone in textile effluent treatment appears as a very attractive alternative with considerable application potential. Ozone is a powerful oxidizing agent ($E° = 2.08$ V), and can react with several classes of compounds through direct or indirect reactions [12]. The chromophore groups generally are organic compounds with conjugated double bonds that can be broken by ozone (directly or indirectly) forming smaller molecules, which decrease the effluent color.

The more complex environmental problems associated with the textile industry are due to wide utilization of carcinogenic or mutagenic reactive dyes, which are resistant to microbial degradation [5]. Some reactive dyes are either toxic or can be modified biologically to toxic or carcinogenic compounds [11]. The nonbiodegradability of textile wastewater is due to its high content of dyestuffs, surfactants and additives. There are no universally useful methods available for treatment of dye wastes, probably because of the complex and very varied chemical structures of these compounds [11].

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* Corresponding author. Tel.: +90 442 231 4601.
*E-mail address:* eoguz@atauni.edu.tr (E. Oguz).

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Since commercial dyestuffs are intentionally designed to be recalcitrant under typical usage conditions, a marked resistance of these dyes to aerobic biological treatment is not unusual [8,9,15].

It was observed that chemical oxygen demand (COD) and biological oxygen demand (BOD) of aqueous dyes decreased after ozonation [10]. It was also reported that COD decreased only in the case of pure dye solution, but for a real wastewater COD remained unchanged and TOC content was also unaffected [3]. This indicates that the dye chromophore degrades to a form that may not decompose further by ozone alone. Ozone is also known to be very effective in removing color caused by water-soluble dyes, particularly fiber acid and reactive dyes [13,14]. However, ozonation has proven to be rather inefficient for the reduction in chemical oxygen demand (COD) or total organic carbon (TOC), usually not exceeding 50 and 40%, respectively, independent of the initial dye concentration [4].

An affordable and easy-operated control technology without the formation of sludge is needed to comply with today's demanding legislation. One choice is advanced chemical oxidation. The use of chlorinated oxidants, such as chlorine dioxide or chloramine, is not suggested as toxic or may result in less biodegradable chlorinated by-products being formed [16]. Ozonation for color removal might be a promising process for the following reasons: (1) no chemical sludge is left in the treated effluent; (2) ozonation has the potential to accomplish both color removal and organic reduction in one step; (3) less space is required, and it is easily installed on site; (4) there is less danger, since no stock hydrogen peroxide or other chemical is required on site; (5) it is easily operated; and (6) all residual ozone can easily be decomposed to oxygen and water.

The main objective of this work was to study removal of dye and COD from Bomaplex Red CR-L textile dye by ozonation. Semi-batch ozonation experiments are realized under the different reaction conditions. The concentrations of the Bomaplex Red CR-L and COD were analyzed as a function of color at specified time intervals. High dye removal efficiency increased with destruction of conjugated double bonds that can be broken by ozone (directly or indirectly). However, the reaction intermediates and products formed during ozonation were not examined. This work focuses on the ozonation of the Bomaplex Red CR-L dye. At the end of this work, the efficiencies of removal of dye and COD from the synthetic textile wastewater were, respectively, 99 and 56%.

## 2. Materials and method

The experimental set-up shown in Fig. 1 consists of an air dryer and compressor, ozone generator and semi-batch reactor. The air dryer consisted of a column which was filled with a high adsorptive anhydrous $CaCl_2$. Ozone was generated using an ozonizer Model OG-24; water was used as the cooling medium. The ozone–oxygen mixture was then fed into the contact place through a porous plate gas sparger located at the semi-batch reactor's base. All experiments were carried out in a 1000 mL cylindrical semi-batch reactor. The reactor had a glass column of 7-cm diameter, 40-cm height and a water cooling jacket to keep the reactor contents at constant temperature. Dye solution of 250 mL was used during each batch ozonation. A magnetic stirrer was used with the gas diffuser to achieve sufficient recirculation of the dye solution.

The Bomaplex Red CR-L dye was obtained from a textile mill located in Türkiye. Solutions of this dye were prepared with distilled water in concentrations of 1000 mg $L^{-1}$. The dye concentration time data during dye and COD removal were detected using spectrophotometry. The dye used in the present work was water-soluble having the structure shown in Fig. 2.

In Fig. 3, it is shown that the Bomaplex Red CR-L dye gave a peak at 505 nm using spectrophotometry as a function of color. Dye removal capacity was determined by absorbance measurements at the maximum visible absorbance wavelength of 505 nm. All the samples to measure dye concentrations were analyzed at 505 nm.

The capacity of COD removal was determined by absorbance measurements at the maximum visible absorbance wavelength of 600 nm. All the samples to measure COD concentrations was analyzed at 600 nm [2].

Ozone was generated from air, and was supplied into the system through an Opal OG-24 model ozonizer at rates of 5, 10 and 15 L $min^{-1}$. $O_3$ was determined by iodometry. Ozonation was performed in a cylindric semi-batch glass reactor (volume 1 L). The Bomaplex Red CR-L dye was ozonated for 30 min in the semi-batch reactor. The ozone–air mixture percentages (0.7, 1.1 and 1.4 $O_3$%) were continuously sparged through a diffuser.

## 3. Results and discussion

Fig. 4 shows the change of the initial dye and COD concentrations (from 400 to 1000 mg $L^{-1}$ and from 285 to 695 mg $L^{-1}$ $O_2$) with time during ozonation. The rate of dye removal was high at the beginning and then decreased with time. The efficiency of dye removal after an ozonation of 30 min did not scarcely increase with increasing initial dye concentration in the wastewater. After an ozonation of 30 min, the efficiencies of dye removal over 99% were obtained. The efficiencies of COD removal were high at the beginning and then decreased. The efficiencies of COD removal did not

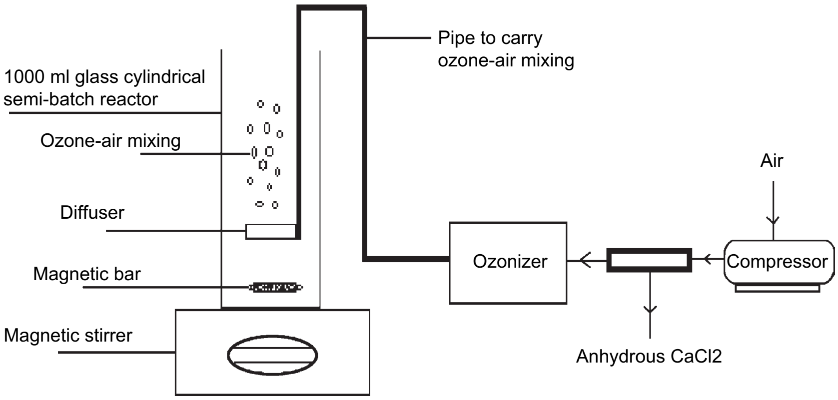

Fig. 1. Diagram of ozonation system.

change with increasing initial COD concentration in the synthetic wastewater. After an ozonation of 30 min, the efficiency of COD removal was approximately 54%.

Fig. 5 shows that dye degradation scarcely changed with ozone–air flow rates (5, 10 and 15 L min$^{-1}$). From Fig. 5 it was understood that ozone–air flow rate of 5 L min$^{-1}$ was an efficient dose to degrade 1000 mg L$^{-1}$ of dye. After an ozonation of 15 min, all the dye in the synthetic wastewater was removed, and obtained a dye removal efficiency of 99%. Fig. 5 also shows that COD concentrations scarcely changed with increasing ozone–air flow rates. After an ozonation of 30 min, the efficiency of the COD removal from synthetic wastewater at different ozone–air flow rates was approximately 54%.

Fig. 6 shows that dye degradation increased with increasing ozonation generation percentage (from 0.7 to 1.4 $O_3$%). The more the double bonds in molecular $O_2$ were broken with increasing ozone generation percentage, the more the molecules of $O_3$ occurred. After the $O_3$ molecules attacked the double bonds in the dye molecules, they were broken by ozone. With more dye molecule degradation, more dye molecules were removed from synthetic wastewater. When the ozonation generation percentage increased from 0.7 to 1.4 $O_3$%, a dye removal efficiency of 99% was obtained at an

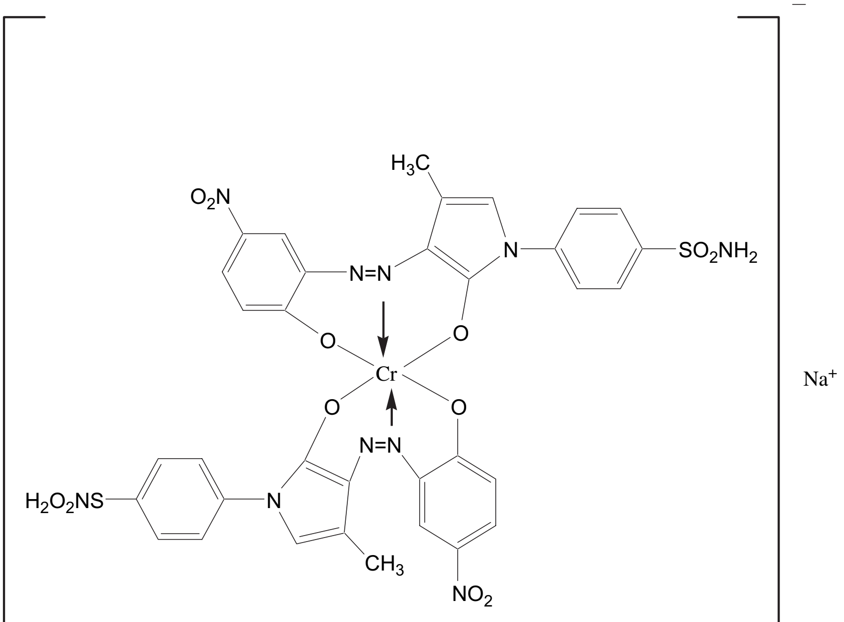

Fig. 2. The general chemical structure of the Bomaplex Red CR-L group dyes.

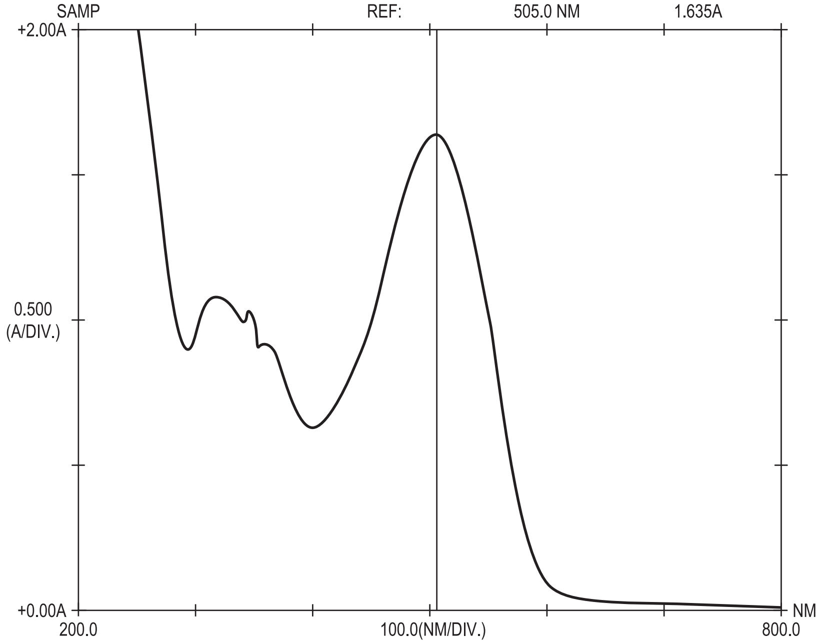

Fig. 3. The spectrum curve of the Bomaplex Red CR-L dye at 505 nm.

ozonation of 15 min. An efficiency over 99% was achieved at the end of the reaction. The mechanism the most referred to for the formation of ozone in the electrical discharges is the following:

$$O + O_2 + M \xrightarrow{k_1} O_3 + M$$

The function of the third element M is to absorb (under kinetic or potential form) the excess energy of the reaction. The constant velocity $k_1$ depends on the nature of the third element and on the state of the excitation of the species involved [6].

Fig. 6 also shows that the efficiency of COD removal increased with increasing from 0.7 to 1.4 $O_3$%. When

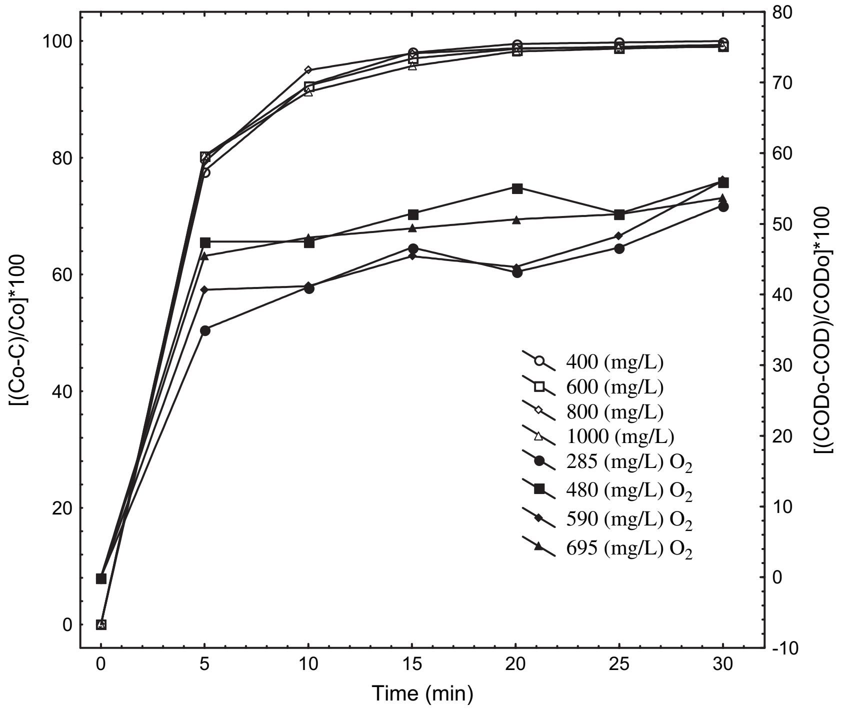

Fig. 4. Effect of initial dye concentrations on the efficiency of dye and COD removal with time (pH: 9.3, $T$: 18 °C, ozone–air flow rate: 5 L $min^{-1}$, ozone generation percentage: 1.4 $O_3$%).

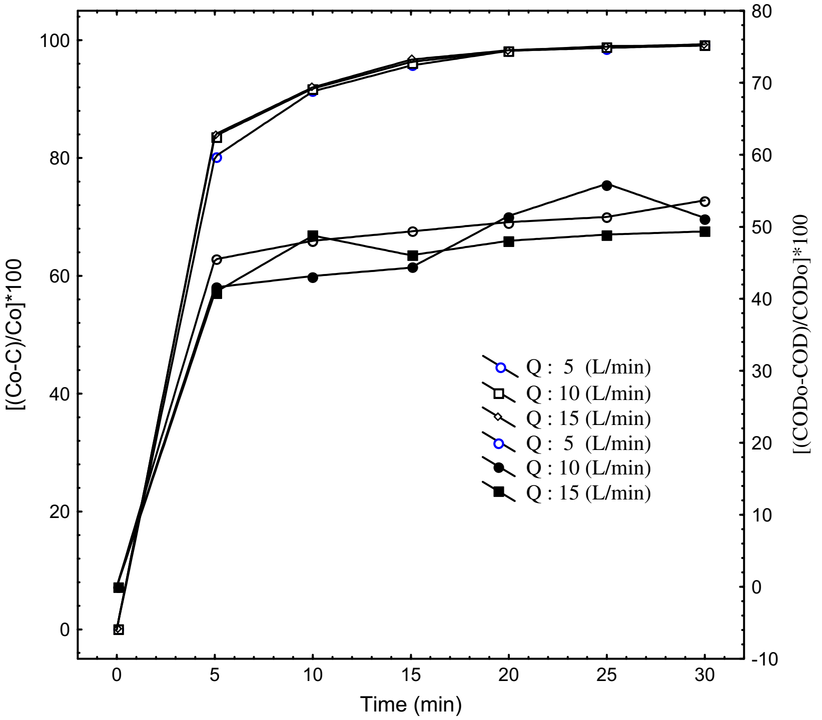

Fig. 5. Effect of ozone–air flow rate on the efficiency of dye and COD removal with time ($C_o$: 1000 (mg $L^{-1}$), $COD_o$: 695 (mg $L^{-1}$) $O_2$, pH: 9.3, ozone–air flow rate: 5 L $min^{-1}$, $T$: 18 °C, ozonation generation percentage: 1.4 $O_3$%).

the ozone generation percentage increased from 0.7 to 1.4 $O_3$%, a COD removal efficiency of 54% was obtained at an oxidation of 30 min. After an ozonation of 30 min, the efficiencies of the COD removal at different ozone generation percentages were 46, 50 and 54%.

The ozonation of dye at various initial pH values (3, 6, 9.3 and 12) was examined, and was shown in Fig. 7.

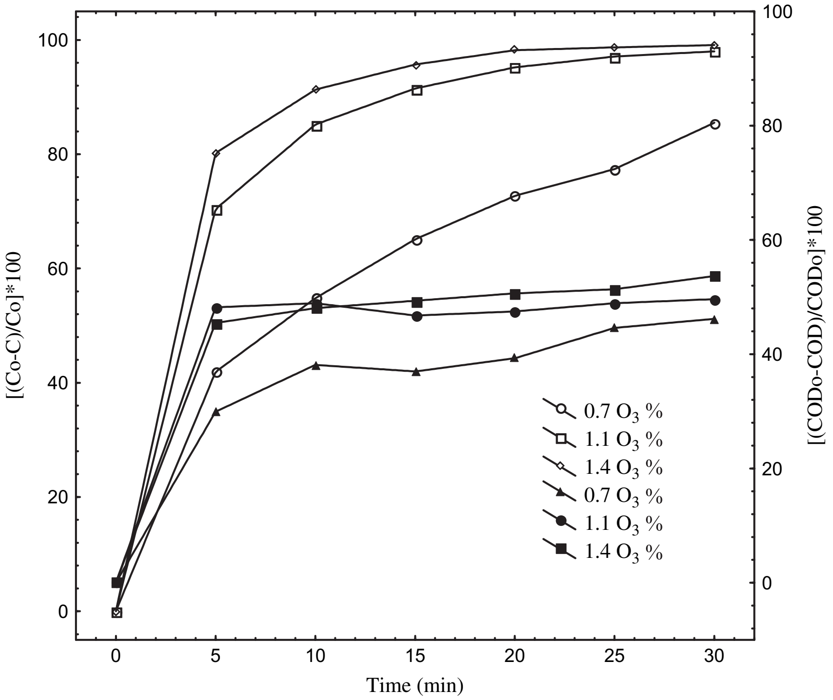

Fig. 6. Effect of ozone generation percentages on the efficiency of dye and COD removal with time ($C_o$: 1000 (mg $L^{-1}$), $COD_o$: 695 (mg $L^{-1}$) $O_2$, pH: 9.3, $T$: 18 °C, ozone–air flow rate: 5 L $min^{-1}$, ozone generation percentage: 1.4 $O_3$%).

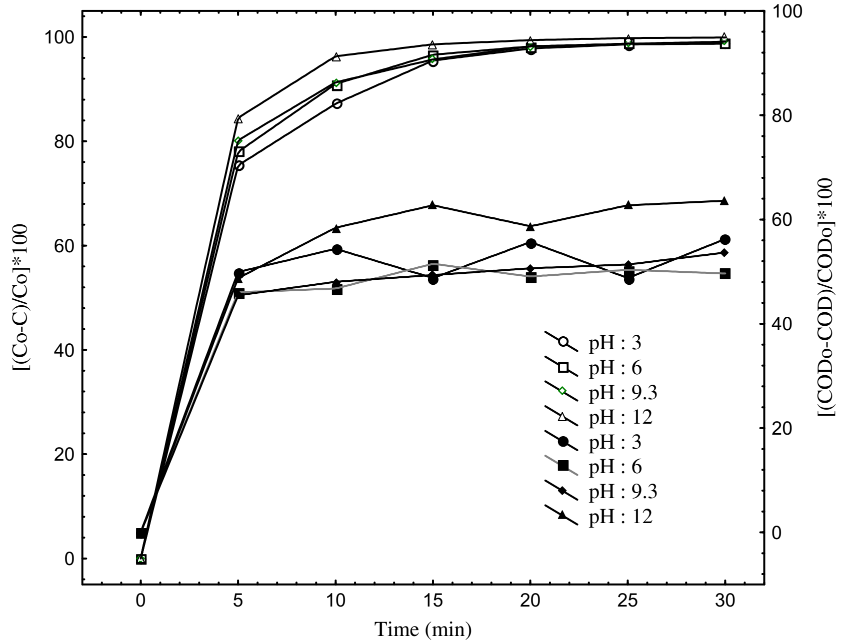

Fig. 7. Effect of pH values on the efficiency of dye and COD removal with time ($C_o$: 1000 (mg $L^{-1}$), $COD_o$: 695 (mg $L^{-1}$) $O_2$, $T$: 18 °C, ozone–air flow rate: 5 L $min^{-1}$, ozone generation percentage: 1.4 $O_3$%).

The degradation of the Bomaplex Red CR-L dye was found to increase with the increasing and decreasing of pH during an ozonation of 10 min. In general, ozone oxidation pathways include direct oxidation by ozone or radical oxidation by $OH^{\cdot}$ radical. Direct oxidation is more selective and predominates under acidic conditions, while radical oxidation is less selective and predominates under basic conditions. Since the oxidation potential of hydroxyl radicals is much higher than that of the ozone molecule, direct oxidation is slower than radical oxidation. The increase of solution pH did not showed a positive enhancement of the ozone oxidation of the Bomaplex Red CR-L dye during an ozonation of 30 min.

The ozonation of the Bomaplex Red CR-L dye at various initial pH values (3, 6, 9.3 and 12) was

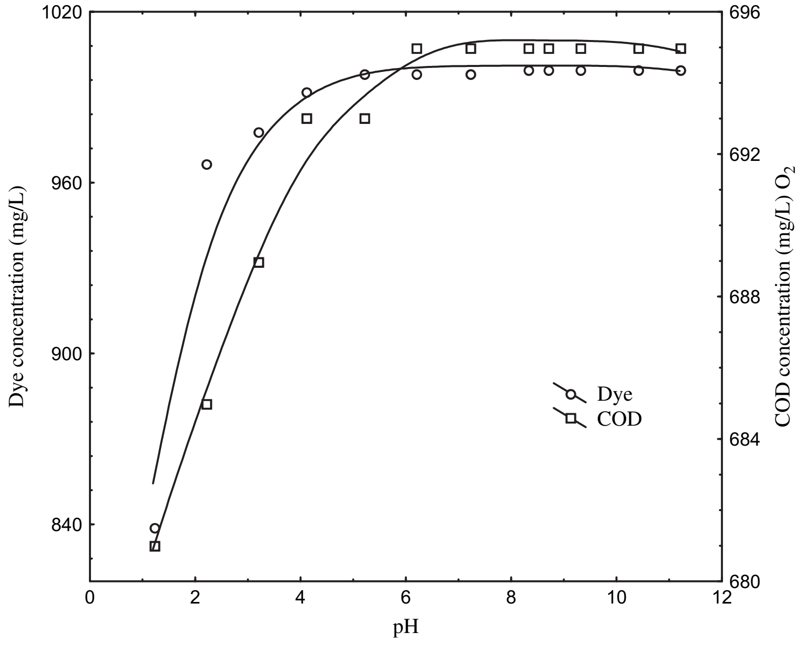

Fig. 8. Effect of pH on the dye and COD without ozonation ($C_o$: 1000 (mg $L^{-1}$), $COD_o$: 695 (mg $L^{-1}$) $O_2$, $T$: 18 °C, time: 30 min).

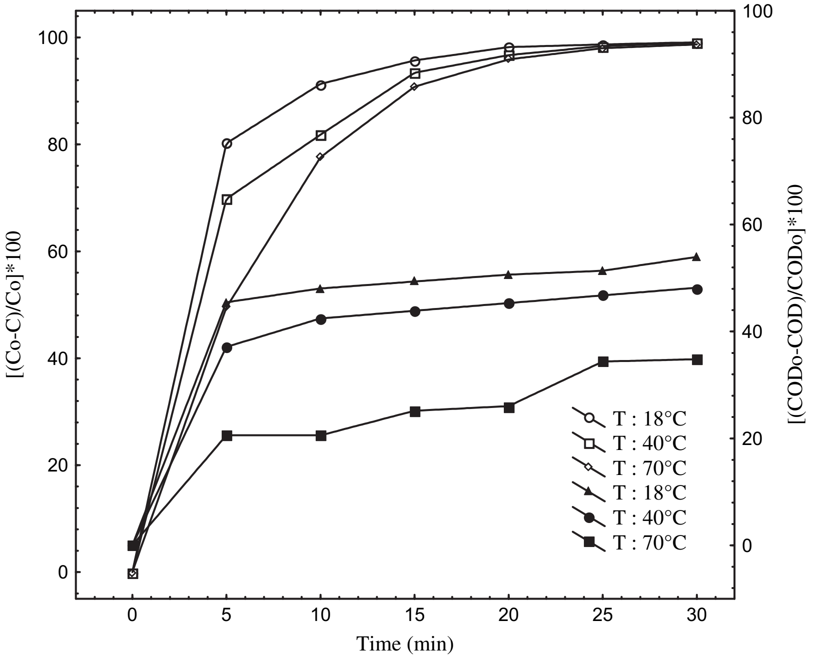

Fig. 9. Effect of temperature range on the efficiency of dye and COD removal with time ($C_o$: 1000 (mg $L^{-1}$), $COD_o$: 695 (mg $L^{-1}$) $O_2$, pH: 9.3, $T$: 18 °C, ozone–air flow rate: 5 L $min^{-1}$, ozone generation percentage: 1.4 $O_3$%).

examined, and was shown in Fig. 8. The COD removal from the Bomaplex Red CR-L dye was found to increase with the increment and decrease of the pH during ozonation. The increase of solution pH did show a positive enhancement for the COD removal from the Bomaplex Red CR-L dye, because of $OH^{\cdot}$ radicals. Besides, the decrease of solution pH also showed a positive enhancement for the COD removal from the Bomaplex Red CR-L dye because of the dye degradation at acidic conditions as seen in Fig. 8.

The Bomaplex Red CR-L dye has a property of a base, and has been degraded at acidic conditions ($pH < 4$). Fig. 8 shows that dye concentration has changed according to acidic pH values. The dye concentration of 15% was degraded at pH 1. Thus, the decrease of synthetic wastewater pH did show

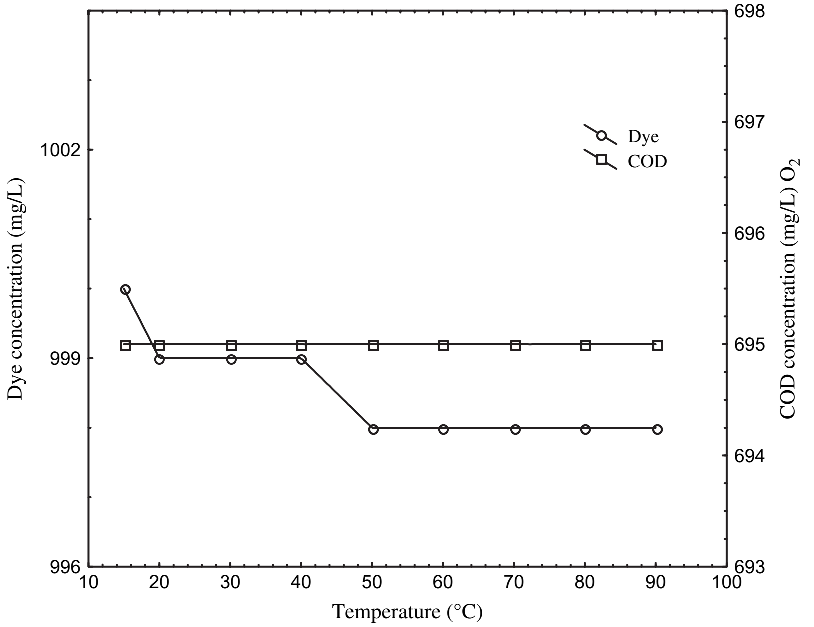

Fig. 10. Effect of pH on the dye and COD removal without ozonation ($C_o$: 1000 (mg $L^{-1}$), $COD_o$: 695 (mg $L^{-1}$) $O_2$, pH: 9.3, time: 30 min).

a positive enhancement of the ozone oxidation of the Bomaplex Red CR-L dye because of dye degradation at acidic conditions as seen in Fig. 8 which also shows that COD removal has changed according to pH values.

Fig. 9 shows that the removal of dye has increased with decreasing temperature ranges. The dye removal efficiencies after an ozonation of 5 min was, respectively, 80, 70 and 52.5% at different temperatures (18, 40 and 70 °C). This decrease in the dye removal efficiencies with increasing temperature was derived from decreasing ozone solubility in solution with increasing temperature, but at ozonation of 15 min, the dye removal efficiencies was almost equal. It seems that the increase in reaction rate with the temperature rise is more significant than the decrease in ozone solubility due to the temperature rise. Fig. 9 also shows that the COD removal has increased with decreasing temperature ranges. The efficiencies of the COD removal after an ozonation of 30 min, respectively, was approximately 54, 48 and 35% at different temperatures ranges (18, 40 and 70 °C). This decrease in the COD removal efficiencies was derived from decreasing ozone solubility in solution with increasing temperature.

Fig. 10 shows the relation between the Bomaplex Red CR-L dye and different temperature ranges of synthetic wastewater. According to Fig. 10, it was determined that dye concentration scarcely changed at different temperature ranges of the synthetic wastewater without ozonation. Besides, Fig. 10 also shows the relation between the COD values and different temperature ranges in synthetic wastewater without ozonation. According to Fig. 10, it was determined that COD concentration did not change at different temperatures in synthetic wastewater without ozonation

## 4. Conclusions

Ozonation is a widely used method of dye removal from textile effluents. The ozonation process lead to complete dye removal with a very short reaction time (typically, 15 min). The dye removal from synthetic wastewater containing Bomaplex Red CR-L dye in a semi-batch reactor by ozone was found to be an efficient technique for textile dyeing wastewater treatment. In this study, the dye removal efficiency of over 99% was obtained at an ozonation of 30 min under different empirical conditions (dye concentration, temperature, pH, ozone–air flow rate and ozone generation percentage). The present study emphasizes that the dye removal by ozonation is a very efficient process. However, the ozonation process did not lead to complete COD removal and was proven to be rather inefficient for the removal of COD, usually not exceeding 54%. In this study, the efficiency of COD removal was approximately 54% at an ozonation of 30 min at the above mentioned empirical conditions. The present study emphasizes that the COD removal from the synthetic textile wastewater by alone ozonation is an inefficient process.

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