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Decolorization and mineralization of C.I. direct red 28 azo dye by ozonation

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ABSTRACT

This study evaluated the efficiency of ozonation for removal of color and chemical oxygen demand (COD) of Congo red, as an anionic dye was selected due to the complex chemical structure with di-azo aromatic group and extended application in the textile industry. The effect of ozonation time on the rate of COD removal, mineralization and rate of decolorization were studied and the result was analyzed in terms of COD and color removal efficiency. Intermediate and final by-products formed during ozonation were identified by ion chromatography (IC). Dye decomposition rate was observed by UV–vis spectroscopy. The removal of COD and color of Congo red by ozonation was performed in a batch reactor with constant ozone flow rate and concentration of 5 g/hr and 55.5 mg/L, respectively. Dye concentration was 1,500 mg/L. Decolorization and degradation of dye sample were carried out with a certain time interval and analyzed immediately. The COD and color removal efficiencies increase at specified time of ozonation. After 15 min of ozonation time, the COD of Congo red was increased. Results with Congo red synthetic dye solution showed the maximum COD reduction of 67%, obtained after 10 min of ozonation. The reduction of COD showed partial degradation of this dye. Ninety percentage of color removal was achieved after 25 min of ozonation time. Dyes are completely destroyed with the formation of final product chloride, fluoride, sulfate, nitrate, and oxalate ions analyzed by ion chromatography. During ozonation process, rapid decrease of pH gave evidence for production of acidic by-products. The effect of buffered solutions (phosphate buffer) on the dye solutions was further investigated in this study. Ozonation also resulted in increase of electrical conductivity of the dye solution.

Keywords: Congo red; Degradation; Mineralization; Decolorization; Ozonation by-products

1. Introduction

Textile industry effluents are complex waste products characterized by high content of dyestuff, salts, high chemical oxygen demand (COD) derived from additives, suspended solids, and variation in pH [1]. Strong color of the textile wastewater is the most serious problem of the textile industry effluents. Textile industry generates highly polluted wastewater because it contains dyes, typical organic compounds with complex structures that are very soluble in water

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and easily hydrolyzed [2,3]. Most of the dye molecules are complex, particularly reactive azo dyes causes special environmental concern due to their degradation products, such as aromatic amines which are highly carcinogenic [4–6]. More than 8,000 chemically different types of dyes are currently manufactured and the biggest consumers of these dyes are the textile industries [7]. He et al. [8] estimated 10–20% of dyes is lost during the dyeing process and released as effluent. Textile industry effluents containing a significant concentration of dyes cause serious treatment problems and it is very difficult to break them down. These textile effluents cannot be treated efficiently by conventional methods or activated sludge treatment or any combination of biological, chemical and physical methods [9]. Advanced oxidation processes are having ability to completely decolorize and mineralize the textile effluents in short reaction time with no sludge production in the end. It could be a viable option for treating dye effluents because it breaks down the aromatic structures [10–12]. Ozonation, as an advanced oxidation process, has been used for treating color water, especially textile industry wastewater [13,14]. It is very effective for decolorizing organic dye wastewaters because it attacks conjugated double bonds of dye molecules. Ozone is useful for removing various toxic chemicals and color from wastewater. It helps decompose detergents, chlorinated hydrocarbons, phenols, pesticides, aromatic hydrocarbon [15] reducing the COD, and total organic carbon (TOC) of wastewater [16–18].

1.1. Ozone mechanism

In general, ozone cleaves the conjugated bonds of dye molecule, resulting in color removal and enhancing biodegradability. Cleavage of dye bonds takes place in ozonation process by two different ways namely direct molecular and indirect radical-type chain reactions. In acidic pH, the ozone is available as molecular ozone which directly reacts in aqueous solution and in alkaline pH ozone decomposes to $OH^{\cdot}$ radicals [19–22]. The free radicals ($HO_2^{\cdot}$ and $HO^{\cdot}$) produced due to the decomposition of ozone, reacts with a variety of impurities. The hydroxyl radical ($OH^{\cdot}$) is a powerful, non-selective chemical oxidant, which acts very rapidly with most organic compounds. A simple mechanism for the decomposition of ozone in aqueous solution is illustrated in following equation [23].

$$O_3 + OH^- \rightarrow HO_2^{\cdot} + O_2^{-\cdot} \quad (1)$$

$$O_3 + HO_2^{\cdot} \rightarrow OH^{\cdot} + 2O_2 \quad (2)$$

$$O_3 + OH^{\cdot} \rightarrow O_3^{\cdot} + OH^{\cdot} \quad (3)$$

$$O_3^{\cdot} \rightarrow O^{\cdot} + O_2 \quad (4)$$

$$O^{\cdot} + H^+ \rightarrow OH^{\cdot} \quad (5)$$

$$OH^{\cdot} + OH_2^{\cdot} \rightarrow H_2O + O_2 \quad (6)$$

The decomposition process of ozone in aqueous solution has been described by Hoigne, Staehelin, and Bader (HSB) model. The decomposition routes of ozone with reaction rate constants are following equation [24,25]:

$$O_3 + OH^- \rightarrow HO_2^{\cdot} + O_2^{-\cdot} \quad k = 70\ M^{-1}s^{-1} \quad (7)$$

$$O_3 + O_2^{-\cdot} \rightarrow O_2 + O_3^{-\cdot} \quad k = 1.6 \times 10^9\ M^{-1}s^{-1} \quad (8)$$

$$H^+ + O_3^{-\cdot} \leftrightarrow HO_3^{\cdot} pK_a = 10.3 \quad (9)$$

$$HO_3^{\cdot} \rightarrow HO^{\cdot} + O_2 \quad k = 1.1 \times 10^5\ M^{-1}s^{-1} \quad (10)$$

$$HO^{\cdot} + O_3 \rightarrow HO_4^{\cdot} \quad k = 2.0 \times 10^9\ M^{-1}s^{-1} \quad (11)$$

$$HO_4^{\cdot} \rightarrow HO_2^{\cdot} + O_2 \quad k = 2.8 \times 10^4\ M^{-1}s^{-1} \quad (12)$$

$$HO_4^{\cdot} \rightarrow H_2O_2 + 2O_3 \quad k = 5 \times 10^9\ M^{-1}s^{-1} \quad (13)$$

$$HO_4^{\cdot} + HO_3^{\cdot} \rightarrow H_2O_2 + O_3 + O_2 \quad k = 5 \times 10^9\ M^{-1}s^{-1} \quad (14)$$

The reaction rate constants of molecular ozone with different organic compounds are also given in Table 1 [26].

Oxidation by ozone is capable of degrading chlorinated hydrocarbon, phenols, pesticides, and aromatic hydrocarbon [27]. Ozonation is one of the most effective means of decolorizing dye wastewater and has

Table 1
Reaction rate constants (k, $M^{-1}s^{-1}$) of ozone vs. hydroxyl radical

Compound	O_3	$OH^{\cdot}$
Chlorinated alkenes	10^3–10^4	10^9–10^{11}
Phenols	10^3	10^9–10^{10}
N-containing organics	10–10^2	10^8–10^{10}
Aromatics	1–10^2	10^8–10^{10}
Ketones	1	10^9–10^{10}
Alcohols	10^{-2}–1	10^8–10^9

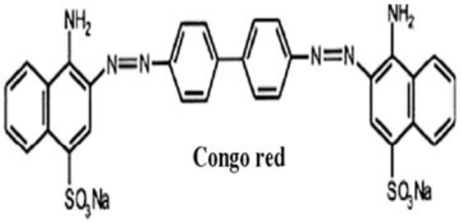

Fig. 1. Chemical structure of Congo red.

been shown to achieve high color and effluent COD removal [28,29]. Amat et al. [30] and Srinvasan et al. [31] documented up to 97% dye color removal by ozonation.

The objective of this study was to investigate the application of ozone for the degradation, mineralization, and decolorization of Congo red, as an azo dye. The effect of ozonation time on the rate of COD removal and rate of decolorization was studied and the results were analyzed in terms of COD and color removal efficiency. This study also identified intermediate and final by-product formed during ozonation. The effect of pH was also assessed using a phosphate buffer solution during ozonation. Ozonation also resulted in increased electrical conductivity of the dye solution studied in the study.

2. Properties of Congo red

Congo red dye is a secondary diazo dye and one of the important textile direct dyes. Its colored substances have complex chemical structures and high molecular weights (696.66 g/mol). Fig. 1 shows the chemical structure of Congo red. It is soluble in water, yielding a red colloidal solution and persistent in the environment, once discharged into a natural environment. Thus, the study on Congo red is noteworthy not only for being possible pollutants of industrial effluents but also because it is a good model of complex pollutants. It makes a strong, though apparently non-covalent affinity to cellulose fibers. Table 2 shows the properties of Congo red. Table 3 shows the characteristics of Congo red dye solution.

3. Materials and methods

3.1. Materials

The studied dye was Congo red, as an azo dye purchased from the commercial market and used without any further purification. It has been selected due to its high solubility in the aquatic environment. Synthetic azo dye solution is prepared by dissolving dye in Milli Q water. The initial pH and concentration of Congo red dye solution has 9.76 and 1,500 mg/L. To evaluate the effect of solution pH, another dyes solution has been prepared by dissolving the dye in phosphate buffer solution pH 7. Characterization of such dyes was conducted like dyes concentration and chemical properties. Carbon content of the solid dye samples was analyzed by CHNOS analyzer model CE40 Elemental Analyzer (Shimadzu) and volatile content of the solid dye samples was analyzed by TOC analyzer model TOC V CPN.

3.2. Ozonation procedure

Ozonation of dye solution was carried out in a batch reactor. Fig. 2 shows the schematic diagram of ozonation apparatus. Ozone was generated by corona discharge-type Ozone Generator model Altech el-5 g/h-A with flow rate of 5 gm/hr from pure oxygen as feed gas. Oxygen was constituted to the ozonator with

Table 2
Properties of Congo red

IUPAC name	Sodium salt of benzidinediazo-bis-1-naphtylamine-4-sulfonic acid
Synonyms	C.I. Direct Red 28
Molecular formula	$C_{32}H_{22}N_6Na_2O_6S_2$
Molecular wt.	696.665 g/mol
C.I. number	22,120
Dye class & type	Anionic, diazo, direct dye
Appearance	Red colloidal
Purity	37.76% (CHN basis)
Absorption maxima	500 nm
Water solubility	Soluble
Melting point	>360˚C
Uses	As dyes in cellulose industry

Table 3
Characteristics of Congo red dye solution

Parameters	Values	Unit
pH	9.76 at 25˚C	–
Chemical oxygen demand	640	mg/L
Total dissolved solids	1,360	mg/L
Total fixed solids	810	mg/L
Total volatile solids	550	mg/L
Color (absorbance)	5 (at 500 nm)	–
TOC (%)	32.35	
Conductivity	2.28 at 25˚C	mS/cm
Dye concentration	1,500	mg/L

a regulated pressure in the cylinder of 120 kg/cm^2, before entering the ozone generator cell. The pressure was set to 2 kg/cm^2 using the pressure regulator of the ozonator. The oxygen gas was distributed through a rotameter. Initial ozone concentration and ozone–oxygen flow rate were 55.5 mg/L and 1.5 LPM, respectively. The initial dye concentration was 1,500 mg/L. The equipment was cooled through air. All the experiments were performed at room temperature. Ozonation was carried out in a 4 L cylindrical Plexiglass bubble column reactor with an internal diameter 9.2 cm and height 60 cm. The volume of synthetic dye sample was used 500 ml. Ozone–oxygen mixture was introduced through a fitted porous diffuser that generates fine bubbles at the bottom of the reactor. The residual ozone in the off-gas was distracted by anhydrous MnO_2. The ozone dose defined as runs of ozone per meter cube of oxygen fed to the ozone generator.

3.3. Analytical methods

Ozone concentration in feed gas was determined by KI starch titration method [32]. Five hundred milliliter of dye solution were prepared using Milli Q water to minimize interference, with an initial dye concentration 1,500 mg/L was added into the reactor before starting the reaction at pH 9.76. Decolorization and mineralization of dyes sample were performed at a certain time interval i.e. experiments were conducted consecutively for contact times of 5, 10, 15, 20, 25 min, and analyzed immediately. The synthetic dye sample was drawn at desired intervals to analyze the variations in pH, conductivity, dye concentration, color, and COD, whereas nitrate, sulfate, and oxalate ions is also analyzed as final by-products in the course of the experiments. Decolorization of dyes sample was measured with the aid of a UV–vis spectrophotometric analysis at the wavelength range of 200–650 nm were performed in order to measure the concentration of dye. The amount of ozone produced and consumed was determined by iodometric method and the extent of mineralization of the Congo red dye sample was assessed by measuring COD described in the standard methods for examination of water and wastewater [33]. The pH and conductivity of synthetic solution were measured by pH Meter Model (EI) 101E and conductivity meter model 145 A+ (Thermo Orion). The dye decomposition as well as the intermediate and final by-product identification have been achieved by ion chromatography (IC) model 845 Compact IC (Metrohom) analyses. Color and COD removal efficiency were determined by following equations (15) and (16):

$$C_{\text{color }\%} = \left(\frac{C_{\text{dye},i} - C_{\text{dye},f}}{C_{\text{dye},i}}\right) \times 100 \tag{15}$$

$$C_{\text{COD}\%} = \left(\frac{\text{COD}_i - \text{COD}_f}{\text{COD}_i}\right) \times 100 \tag{16}$$

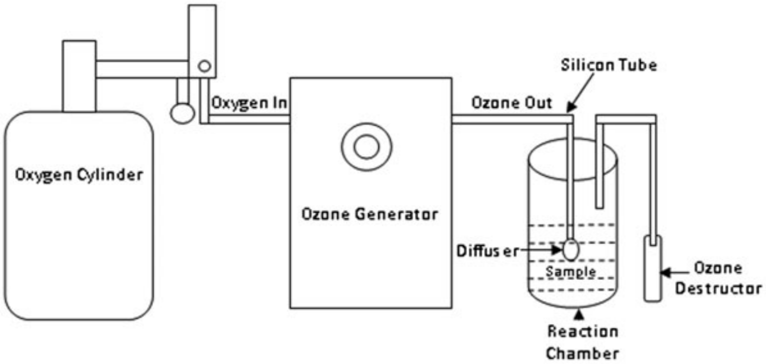

Fig. 2. Diagram of ozonation procedure.

where C_{dye} (mg/L) is the dye concentration and COD (mg/L) is the chemical oxygen demand of the dye solution, whereas "*i*" and "*f*" correspond to initial time and the final sampling time of the ozonation treatment.

4. Results and discussion

4.1. Effect of ozonation contact time on pH

As ozonation was conducted into a batch reactor, the pH of dye samples was decreased. Fig. 3 shows the variation in pH at 25˚C with ozonation time for initial dye concentration of 1,500 mg/L. This indicates that the initial pH values decreased rapidly with ozonation time, from 9.76 to 2.69 in 25 min. These variations in pH are due to the formation of organic and inorganic acids; as the system approached a steady state, the pH reached a constant 2.69 ± 0.1 as shown in Fig. 3. It can be noted that the by-products of acidic nature was generated (inorganic acids and organic anions), as a result of oxidation by ozone. According to references, Alvares et al. [34] and Soares et al. [35] observed that the oxidation by ozone is directly affected by the solution pH. The pH is part of the major factors which affect treatment efficiency by ozonation. Ozone reacts with aromatic pollutants found in water and wastewater via two distinct pathways, namely direct and indirect pathways of reaction. In direct ozonation, molecular ozone as the main oxidant at low pH, while in the indirect pathway, hydroxyl radicals are formed from ozone decomposition at high pH values. Faria et al. [36] observed that the solution pH decrease to values characteristic of organic acids formation, whose by-products are resulted from dyes solution treatment by ozone. The reaction of ozone both with hydroxyl anions and the products of degradation formed by oxidation via hydroxyl radicals tend to decrease the pH of the solution during treatment. The decrease in pH is very pronounced in the initial phase of the process (particularly for alkaline solutions) because there is a greater ozone consumption and dye degradation/mineralization.

To evaluate the effect of pH, additional experiments were carried out with pH 3 and phosphate buffer solution at pH 7 under similar conditions. The result proves that with pH 3 there is no significant difference until relatively stable values are reached, close to those observed for the other initial pH values. In case of buffer solution at pH 7, the solution pH did not change with time during ozonation in spite of buffering of the dye solutions to resist change in pH. It was observed that in unbuffer case, the pH value decrease with the ozonation time until a steady state was reached, which was indicative of the generation of by-products of an acid nature as a result of the oxidation by ozone.

4.2. Effect of ozonation contact time on dye concentration

Fig. 4 shows the results of the reduction in the dye concentration during ozonation of Congo red dye solution with an initial concentration of 1,500 mg/L. It can be observed that for a longer ozonation times, there is a greater reduction in the Congo red dye concentration. In the dye molecules, ozone selectively attacks the electron-rich sites i.e. the aromatic rings and azo bonds, resulting in dyes degradation. Reaction time for 25 min is an initial dye concentration of 1,500 mg/L result shown around 90% of the original dye present in the solution could be destroyed by ozonation. Degradation of high concentration Congo red dye molecules required longer ozonation time.

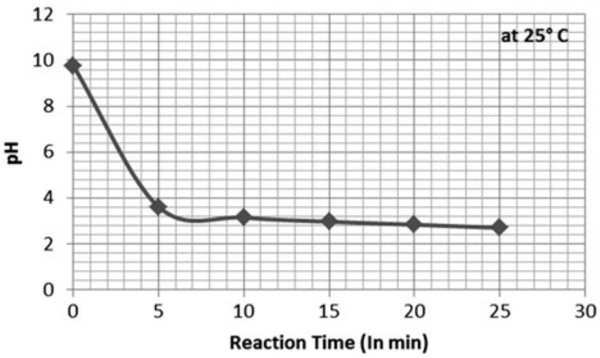

Fig. 3. Variation in pH at 25˚C with ozonation time for dye concentration of 1,500 mg/L.

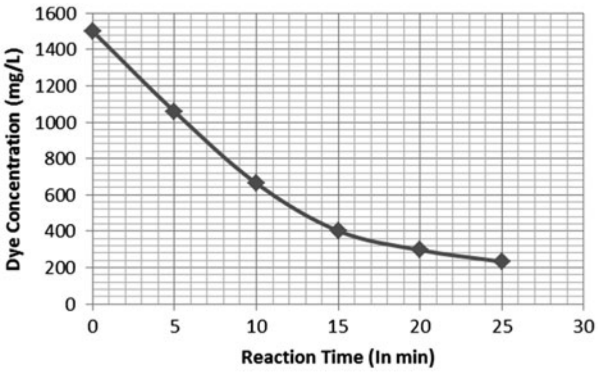

Fig. 4. Dye concentration reductions during ozonation of Congo red dye solution with an initial concentration of 1,500 mg/L.

4.3. Effect of ozonation contact time on the dye decolorization

Analysis of the results indicated that ozonation contact time had a significant effect on color removal. The colorants decomposition dynamics were obtained by UV–vis absorbency at 200–650 nm. The dyes decoloration dynamics were obtained by UV–vis spectrum at 500 nm for Congo red. According to bibliographic data [37], the first stage of decoloration, the reaction of ozone with a single chromophore group such as an azo group connecting aromatic rings. Fig. 5 displays the decolorization of Congo red dye solutions after 25 min of ozonation. From result, we observed that the color reduction occurred very fast achieving around 56% decolorization in 10 min at pH 3. After 25 min treatment time, the color reduction reached 90%. High color removal is achieved at low pH. These observations are well supported by Maciejewska et al. [38] and concluded that in acidic solution, the dyes ozonation is performed by the direct mechanism. The degree of decoloration is favored by direct ozone attack, at low pH, since molecular ozone selectively attacks chromophore groups. Hydroxyl radicals have a greater oxidative power and are less selective than molecular ozone, leading to a decrease in decolorization and an increase in mineralization at higher pH. Color removal and dye degradation data taken together indicates that ozonation resulted in destruction of dye molecules with the formation of by-products. This observation indicates that the color removal can be achieved in a simple process via both reaction pathways of ozone with Congo red mainly at low pH. The results achieved in the present study show that color disappears mostly for Congo red dyes after 10 min of ozonation and achieved high decoloration. A rapid decline in absorbance shows the decoloration dynamics as shown in Fig. 6.

Fig. 7 shows the UV–vis spectrum of Congo red dye before and after ozonation treatment at 200–650 nm. The peak for the Congo red dye solution was observed at $\lambda_{\max}$ of 500 nm. The specified wavelength peak disappeared after ozonation, which indicated that the azo group of the synthetic dyes was transformed by ozonation. The visible spectrum shows that the dye decolorization through cleavage of the chromophore group, where azo dyes are characterized by the –N=N– bond. It can be observed from Fig. 7 that the dye is destroyed by ozone very rapidly with the formation of organic acids (Fig. 3 gave evidence). From Fig. 6, it is noted that absorbance reduces progressively with ozonation and it is an evidence of degradation for the aromatic fragments of the dye molecules and oxidation of their intermediates. Alvares et al. [34] presented the cleavage of the chromophore group and suggested that color removal is the first step of partial oxidation. For Congo red dye, similar tendency can be observed.

4.4. Effect of ozonation contact time on the COD removal

Fig. 8 shows the results for COD removal efficiency during ozonation of Congo red dye solution at 1,500 mg/L dye concentration. The results show that ozonation contact time had a significant effect on COD removal. From Fig. 8, we can observe the decrease in COD with increasing ozonation time. Fifty percentage COD removal occurred in 5 min of ozonation time, although in some cases the values of COD increase with increasing ozonation time. In this study, COD increases after 15 min. Fahmi et al. [39] reported that increases of COD were observed in the ozonation

Fig. 5. Decolorization of Congo red dye solutions.

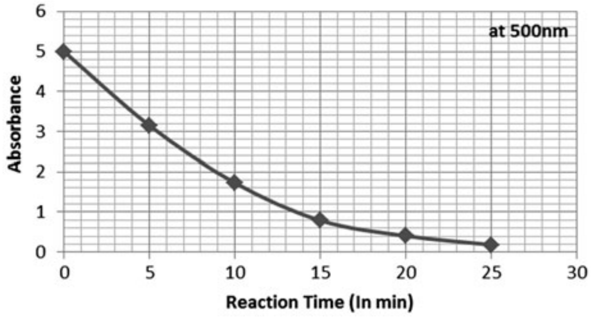

Fig. 6. Dyes decoloration dynamics of Congo red.

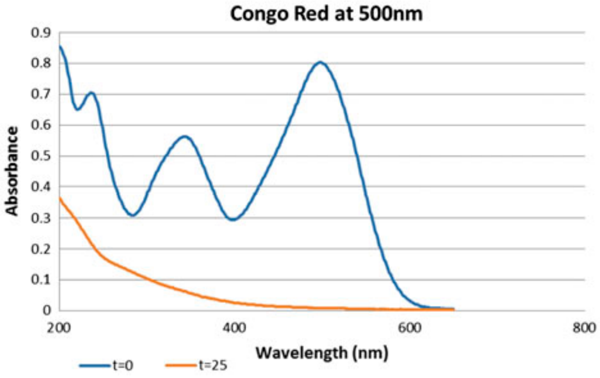

Fig. 7. UV–vis spectrum of Congo red dye solution before and after ozonation treatment.

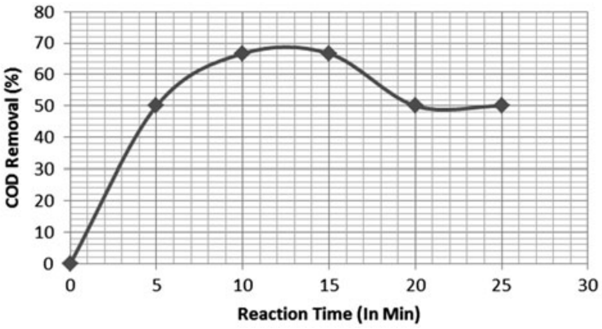

Fig. 8. COD removal efficiency during ozonation of Congo red dye solution at 1,500 mg/L dye concentration.

process due to dye molecules being oxidized resulting in formation of small organic molecular fragments, such as acetic acid, aldehydes, and ketones (as intermediate by-products) which are not completely mineralized under the oxidative conditions, contributing to the increase in COD during ozonation. The optimal ozonation contact time for the maximum observed removal of COD up to 67% was 10 min for an initial concentration of 1,500 mg/L. According to Wang et al. [40], Zou and Zhu [41], Constapel et al. [42] reported that increases of COD is mainly because of an organic species produced following the destruction of the molecular structure of dye by ozonation treatment.

COD removal efficiency increases with an increase in pH of the solution. The maximum removal of COD was observed at high pH, because at high pH more ozone consumption results in more dye degradation. After some time of ozonation, the pH decline due to generation of organic species. According to bibliographic data [40–42], some of the organic compounds were not completely degraded, which is likely due to the fact that some dyes can produce carboxylic acids when directly attacked by ozone (at low pH), and this organic product cannot be oxidized by ozone alone resulting in increasing COD of solution. In this regard, Langlais et al. [25] reported a decline in aromatic structures in organic molecules due to ozonation, with a consequent increase in aliphatic groups containing –COOH, –OH, and –CHO functional groups. In general, aliphatic structures contain higher oxidation state carbon than carbon atoms in the aromatic rings. It should be noted that more than 50% abatement was achieved within the first 5 min at high pH, after that the solution pH decreases with the time and the rate of COD removal also decreases. It can be observed that in high pH condition, COD removal significantly increases likely because alkaline pH accelerated COD removal by generating $OH^{\cdot}$ radicals. A hydroxyl radical is especially important because of its high oxidation potential than ozone molecule (2.8/2.08) [23,43,44].

5. Formation of ozonation by-products

Ozone treatments of wastewaters are complex and often develop a wide range of unstable oxidation by-products, usually oxygenated and polar. During ozone treatment, various intermediates formed upon degradation of the parent dye may interfere with the oxidation. According to bibliographic data [37,45] the intermediates and final products of the dyes ozonation reaction depend on dye chemical structure. High dye concentration formed high level of degradation intermediates by-products [46]. In the present study, intermediates from ozonation are completely destroyed after 15 min and final by-products chloride, fluoride, sulfate, nitrate, and oxalate ions were analyzed by ion chromatography. Perkins [37] suggested that the presence of amino groups in dye molecules is associated with more rapid ozone reaction, while for the sulfonic groups, a resistance increase of dye to an electrophilic attack by ozone.

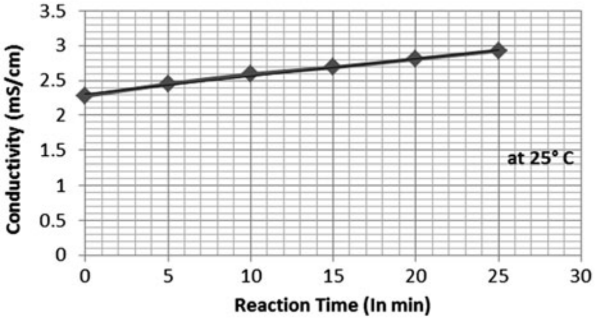

Fig. 9. Conductivity variation at 25˚C of the Congo red dyes solutions during ozonation.

The pH value decreases during ozonation (Fig. 3) as an indirect confirmation test of the organic acids formation in the dyes decomposition. The reaction of ozone both with hydroxyl anions and the products of degradation formed by oxidation via hydroxyl radicals tend to decrease the pH of the solution during treatment. In present study, the absorbance decreases, and this indicates the formation of new compounds or breaking of these molecules into simpler ones. During this process, more complex non-biodegradable compounds are converted to simpler products that contain in their chemical structure an increased percentage of oxygen in the form of hydroxyl, carboxyl, or aldehyde functional groups as intermediates by-products.

In this study, the increase of the dyes solution conductivity after ozonation may serve as an indirect confirmation of sulfate and nitrate ions accumulation. Before ozonation process, the conductivity of the solution was 2.280 mS/cm. After 25 min of ozonation, the conductivity reached 2.93 mS/cm. Fig. 9 represents the conductivity variation at 25˚C of the Congo red dyes solutions during ozonation. The conductivity dynamics for Congo red depend on the chemical structure of organics and on the stoichiometry of the reaction with ozone.

On the other hand, sulfate, nitrate, and oxalate ions were found to be final reaction products. Fig. 10 shows the IC result of fluoride, chloride, sulfate, nitrate, and oxalate ions concentration in dye solutions. Nitrate ions were the main oxidation by-products. These ions were found after the treatment of Congo red dye by ozone and were consistent with CSO_4^{2-}, CNO_3^- and oxalate reached 9.50, 188.34, and 101.07 mg/L, respectively, after 30 min. Further ozonation increases the final by-products concentration. The presence of fluoride and chloride ions in Fig. 4 shows the impurities in dyes. In this study, dye solutions were prepared by dissolving the dye in Milli Q water used without any further purification at concentration of 1,500 ppm. It can be possible to conclude that the commercial dye samples were primarily adulterated with inorganic constituents. High electrical conductivity of the dye

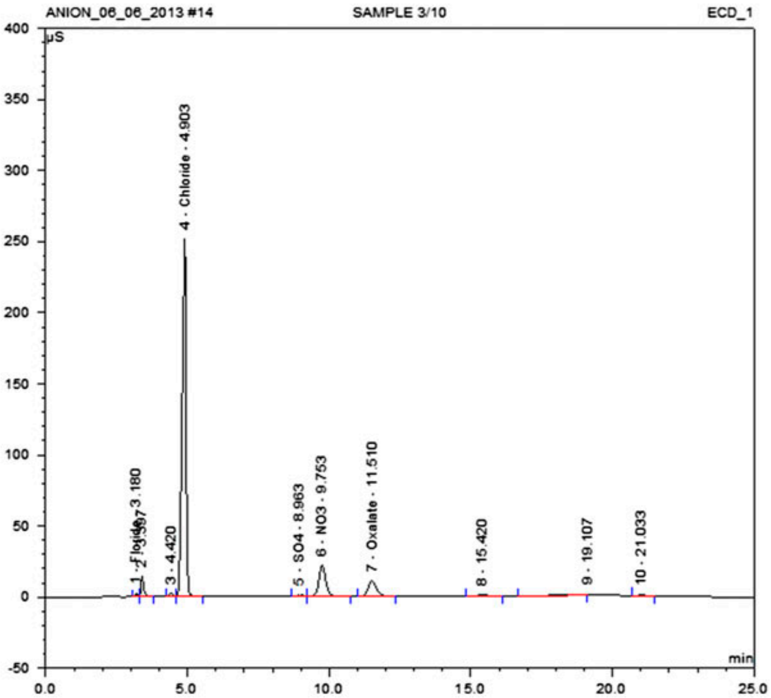

Fig. 10. The IC result of fluoride, chloride, sulfate, nitrate, and oxalate ions concentration in Congo red dye solutions.

Table 4
Electrical energy required by ozonation for color removal at dye concentration 1,500 mg/L of Congo red

Dye concentration 1500 mg/L		
Reaction time	Color removal	EE/O (kWh/m^3)
25 min	90%	113.23

solutions indicated that these inorganic constituents were predominantly ionic in nature.

6. Energy consumption and operating cost of treatment process

The operating costs for different treatment processes vary widely depending on the wastewater flow rate, types, and concentrations of contaminants present, and the degree of removal required. The EE/O, i.e. electrical energy required removing a pollutant by one order of magnitude in 1 m^3 of water or wastewater, is a powerful scale-up parameter which demonstrates a direct link to the electrical efficiency of treatment processes. EE/O is used to measure the treatment rates obtained in a fixed volume of contaminated water as a function of the applied specific energy [47]. Energy consumption and cost of the treatment process depend on the initial dye concentrations, and as well as on the applied dose of treatment. EE/O values have been calculated by implementing the following empirical equation (17) [48]:

$$\mathrm{EE/O} = \frac{P(\mathrm{kW}) \times t(\mathrm{min}) \times 1{,}000}{V(\mathrm{L}) \times 60 \log\left(\frac{C_i}{C_f}\right)} \tag{17}$$

where P, the power input of the ozone generator in kW; t, oxidation time in minutes; V, the volume of the effluent in liters; C_i, initial concentration of contaminant; C_f, the final concentration of contaminant.

Table 4 shows the electrical energy requirements by ozonation for color removal at dye concentration 1,500 mg/L of Congo red. EE/O provides the requisite data for scale-up and economic analysis for comparison with conventional treatment.

7. Conclusions

Ozonation is one of the most effective means of decolourizing dye wastewater and has been shown to achieve high color and effluent COD removal. Oxidation by ozone is capable of degrading and decolorizing organic dye wastewaters because it attacks conjugated double bonds of dye molecules. The decolorization and mineralization of Congo red dye by ozone oxidation were carried out in a batch reactor. The conclusions from this study are that the initial pH values decreased with ozonation contact time, which is indicative of the generation of by-products with acidic nature (inorganic anions and organic acids) as a result of oxidation by ozone. The dyes concentration decrease with increasing ozonation time. The maximum decolorization of Congo red takes place in acid condition, i.e., the direct pathway of ozonation reaction. High color removal achieved at 25 min of ozonation. COD concentration for Congo red dye was decreased significantly up to ozonation time 20 min, whereas further ozonation was not efficient for COD reduction, 67% COD removal achieved at 10 min of reaction time, although increase in COD concentration was observed with increase in ozonation time due to the formation of small aliphatic groups containing –COOH, –OH, and –CHO functional groups as ozonation by-products of oxidation of Congo red dye molecules during ozonation which contributing to the increase in COD. The partial mineralization of dyes occurs after 15 min of ozonation. During ozone treatment, various by-products formed upon degradation of the parent dye. The final products of the dyes ozonation are inorganic and organic ions such as sulfate, nitrate, and oxalate ions detected by IC. Ozonation resulted in increase in conductivity which was partly attributed to the formation of inorganic ions as the organic sulfur and nitrogen in dye molecules were oxidized to inorganic ions during ozonation and it is also due to the formation of depreciated organic acid groups as ozonation by-products of the dye molecules.

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