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Enhancement of biodegradability by continuous ozonation in Acid Red-151 solutions and kinetic modeling

Fulya Gökçen, Tülay A. Özbelge *

Department of Chemical Engineering, Middle East Technical University, 06531 Ankara, Turkey

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Abstract

In this work, continuous ozonation of aqueous Acid Red-151 was performed in a stirred tank reactor at neutral pH and 25 °C. The results show that ozonation is capable of a rapid conversion of the Acid Red-151 dye molecule to more biodegradable intermediates up to the ozonation time of 120 min at which the optimum BOD_5/COD ratio is obtained. The peak BOD_5/COD ratios were found to be in the range of 0.028–0.35 for the initial dye concentrations being in the range of 1000–100 mg/L, respectively.

The proposed kinetic modeling by Liakou et al. [S. Liakou, S. Pavlou, G. Lyberatos, Ozonation of azo dyes, Water Sci. Technol. 35 (4) (1997) 279–286; S. Liakou, M. Kornaros, G. Lyberatos, Pretreatment of azo dyes using ozone, Water Sci. Technol. 36 (2–3) (1997) 155–163] for another azo dye, namely Orange II, could be satisfactorily applied here, to the continuous ozonation of Acid Red-151, which allowed the prediction of the key variables measured experimentally, regardless of the particular intermediate compounds generated during ozonation.

Keywords: Biodegradability enhancement; Azo dye oxidation; Continuous ozonation; Acid Red-151 oxidation; Kinetic modeling; Optimum (BOD_5/COD) ratio

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1. Introduction

Dye molecules present in textile wastewaters are generally high structured polymers comprising two key components: the chromophore that constitutes the colour, and the functional group, which bonds the dye to the fiber. Large amounts of structurally diverse dyestuffs are used in textile industry. Dyes are classified as azo dyes, anthraquinone dyes, triarylmethine dyes, phtalocyanine dyes, etc., with respect to their chemical structures. Generally, azo dyes contain between one and three azo linkages (−N=N−), linking phenyl and naphthyl radicals that are usually substituted with some functional groups such as: amino ($-NH_2$), chloro (−Cl), hydroxyl (−OH), methyl ($-CH_3$), nitro ($-NO_2$) and sulfonic acid sodium salt ($-SO_3Na$). The presence of the sulfonyl group renders the dye readily soluble in water and capable of dyeing wool and silk [1,2]. Ozonation is capable of decomposing the highly structured dye molecules into smaller ones, which can easily be biodegraded in an activated sludge process [3]. Moreover, ozonation process is found to be very effective in decolourization of textile wastewaters by many researchers [4–6]. In this work, a synthetic azo dye, Acid Red-151 has been chosen as a representative model compound used in the textile industry; its continuous ozonation was carried out to compare the present results with those of Orange II in the literature [1,2].

2. Materials and methods

2.1. Experimental

The experimental set-up used in this study is shown in Fig. 1. Dry air is fed to the Fischer OZ-502 type ozone generator. The flow rate of dry air is monitored by a flow meter incorporated with the ozone generator that is 140 L/h, being the optimum value [7,8]. Ozone is sent to the stirred tank reactor (Gallenkamp Modular type) through a sparger. Volume of the stirred tank reactor is 1 L. A Memmert WBU-45 (Germany) type water bath is used to keep the temperature constant at 25 °C. A WTW-310 pH meter is used to control the pH throughout the ozonation process. Ozone traps containing 2% KI solutions are used at the inlet and outlet of the reactor to determine the gaseous ozone concentrations. Experimental parameters are:

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* Corresponding author. Tel.: +90 312 210 2621; fax: +90 312 210 1264.
E-mail address: tozbelge@metu.edu.tr (T.A. Özbelge).

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Nomenclature

a, b	conversion factors
BOD_5	biological oxygen demand measured in 5-day test (mg O_2/L)
C_{dye}	dye concentration (mg/L)
$C_{dye,i}$	initial dye concentration (mg/L)
C_A	Acid Red-151 concentration in modeling equations, or C_{dye} (mg/L)
$C_{O_3\,(liq)}$	dissolved ozone concentration (mg/L)
$C_{O_3\,(gas)}$	ozone concentration in the gas phase (mg/L)
COD	chemical oxygen demand (mg O_2/L)
DOC	dissolved organic carbon (mg C/L)
H	Henry's law constant (atm)
H	Henry's constant in Eq. (16) (L.liq./L.gas)
I_i	model parameters (L/(mg min))
k_i	rate constants (L/(mg min))
$k_l a$	dimensionless ozone mass transfer coefficient
q_g	air flow rate (L/min)
t	ozonation time (min)
TOC	total organic carbon (mg C/L)
V_l	reactor volume (L)
Greek letter	
ν_i	stoichiometric coefficients

- air flow rate (140 L/h);
- temperature (25 °C);
- pH (7);
- initial dye concentration (100, 250, 500 and 1000 mg/L);
- initial dissolved ozone concentration.

Experimental work was undertaken in order to develop a study parallel to that by Liakou et al. [1,2], in which they investigated the continuous ozonation of another azo dye, namely Orange II, at the similar experimental conditions. The present data were used in order to obtain the model parameters for Acid Red-151 to check the applicability of the proposed model to the other azo dyes. Chemical structure of Acid Red-151 is given in Fig. 2.

In these experiments, 50 mL of KH_2PO_4–NaOH buffer solution was prepared and diluted to 1 L with distilled water to be used in adjusting the pH to 7. Then, the amount of dye to provide the desired initial dye concentration in the reactor was added to the stirred tank reactor, which was placed in a water bath at 25 °C. The gaseous ozone produced from dry air was sent to the reactor continuously through a sparger, at a flow rate of 140 L/h. After starting the ozone gas flow into the reactor, the liquid samples were withdrawn from the reactor at definite time intervals. At each definite time, two liquid samples were withdrawn from the reactor simultaneously into two glass bottles, one of which containing 5 mL of 0.01 M $Na_2S_2O_3$ to stop the reaction of ozone with the remaining dye molecules, and the other containing 1 mL indigo reagent plus 10 mL of buffer solution for a pH of 2 to determine the residual ozone concentration in the aqueous medium. All the samples were withdrawn into the sample bottles operated under vacuum in order to prevent the escape of ozone into the gas phase. After the 180th minute, ozone flow was stopped and the ozone generator was shut down. During ozonation, solution pH in the reactor tended to decrease; pH was kept constant at 7, by adding 0.1N NaOH. After the reactor was shut down, volumes of the samples were measured and recorded for the calculations.

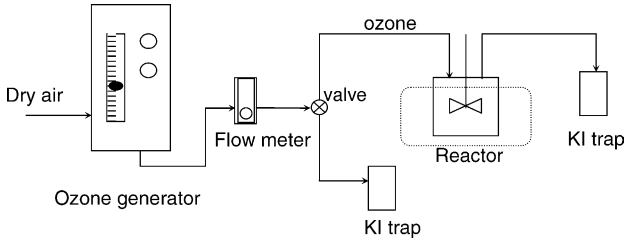

Fig. 1. Experimental set-up for continuous ozonation.

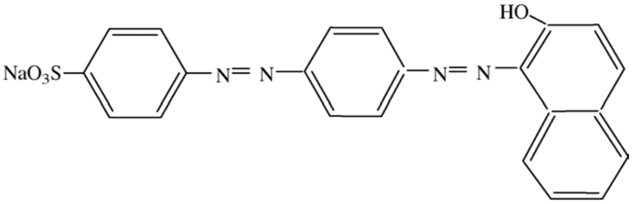

Fig. 2. Chemical structure of Acid Red-151.

The samples withdrawn into 5 mL of thiosulfate solution were used in the measurements of dye concentration and COD. The possible interference of added excess $Na_2S_2O_3$ to the COD measurements was corrected by subtracting the COD value corresponding to the excess $Na_2S_2O_3$ (found by means of the calibration curve of $Na_2S_2O_3$ versus COD) from the measured total COD of the sample. After determining the dissolved ozone concentrations in the dye solution at certain times during ozonation, the amounts of thiosulfate necessary to react with measured values of residual (dissolved) ozone were calculated. At the same initial dye concentration, ozonation was repeated exactly at the same conditions by adding just enough thiosulfate into the flasks according to the calculated amounts to react with the residual ozone. This was because, the excess thiosulfate left in the sample interfered with the BOD_5 measurements; therefore, the thiosulfate solution was added into the flasks in just sufficient amounts so that no excess thiosulfate was left after its reaction with residual ozone in the sample. In the repeated run, the samples were used in the measurements of the dye concentration, COD, BOD_5 and colour. The COD measurement in the repeated run was compared with the COD value obtained by correction using the calibration curve of $Na_2S_2O_3$ versus COD. This gave an idea about the uncontrollable deviations between the two runs at the same conditions. Effluent gaseous ozone from the reactor was trapped in 2% KI solution to determine its concentration by KI method [9] at different times. Inlet gaseous ozone concentration was also measured by KI method after the last sample at the 180th minute was withdrawn from the reactor. Thus, by difference, the ozone consumptions corresponding to different times from the start of the reaction were determined. Before turning off the ozone generator, the tube that carried ozone gas into the reactor was immersed into a gas-washing bottle that contained 2% KI solution. Finally, the ozone generator was turned off and dry air-flow was stopped.

2.2. Analytical methods

Dye concentrations in the solution were determined spectrophotometrically in the visible region at 512 nm corresponding to maximum absorbance wavelength of Acid Red-151 by using a Hitachi U-3010 spectrophotometer. With the same instrument, the residual ozone concentrations in water were determined by Indigo method [10] at 600 nm. COD analysis was performed using a thermoreactor (WTW-3000) and Hach DR-2010 spectrophotometer according to the Standard Methods [9]. Also for colour measurements, Hach DR-2010 spectrophotometer was used [9].

3. Results and discussion

3.1. Colour and COD removals

During ozonation of Acid Red-151 solutions for 180 min, achieved dye eliminations were very high; as shown in Fig. 3, dye concentrations of the ozonated Acid Red-151 solutions approached to zero at the end of 180th minute. All the colour removal percentages at the end of 3 h of continuous ozonation were found to be over 99%. Fig. 4 represents the COD variations in Acid Red-151 solutions with ozonation time.

The COD removals (range of 57.3–73.9%) were not as high as the colour removals; this can be due to the generation of colourless oxidation products which still have some COD while they have no effects on colour.

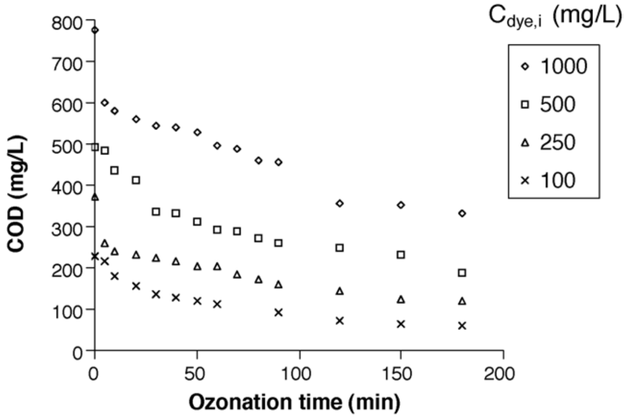

Fig. 4. COD vs. ozonation time at different initial concentrations of Acid Red-151.

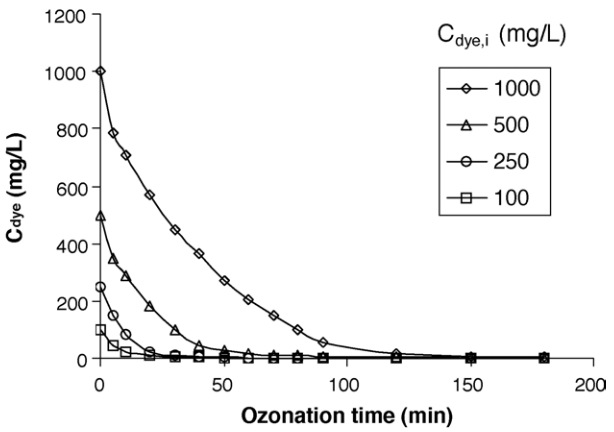

Fig. 3. C_{dye} vs. ozonation time at different initial concentrations of Acid Red-151.

3.2. Enhancement of biodegradability

In the literature, BOD_5/COD, BOD_5/TOC and BOD_5/DOC ratios are used to indicate the biodegradability of wastewaters [11–14]. COD and BOD_5 variations with the ozonation time are obtained for four different initial dye concentrations (e.g. 100, 250, 500 and 1000 mg/L). The one obtained at $C_{dye,i}$ = 500 mg/L is shown in Fig. 5, as an example. As seen in Fig. 5, an increase in the BOD_5 values accompanied a corresponding decrease in the COD values, which indicated the conversion of the dye molecule to more biodegradable compounds; that was also reported by Liakou et al. [1,2]. However, throughout ozonation, after a peak value of BOD_5/COD ratio at an ozonation of 120 min, this ratio starts to decrease (see Fig. 5), which can be explained with further oxidation of the biodegradable products to some gaseous end products or other oxidation products having still some COD [12]. The maximum BOD_5/COD ratio indicates that there is an optimum condition for the enhancement of biodegradability in the ozonation of Acid Red-151. The maximum BOD_5/COD ratio occurred at 2 h of ozonation for Acid Red-151, while this time was given as 1.5–2 h for organics, 1.5 h for Orange II, and 4–5 h for Congo Red [12].

The degree of enhancement in biodegradability of Acid Red-151 solutions decreases with the increasing initial dye concentration with a decrease in the peak value of BOD_5/COD ratio. This could be due to the further oxidation of the generated products after most of the Acid Red-151 was oxidized into smaller molecules. In other words, at low initial dye concentrations, the

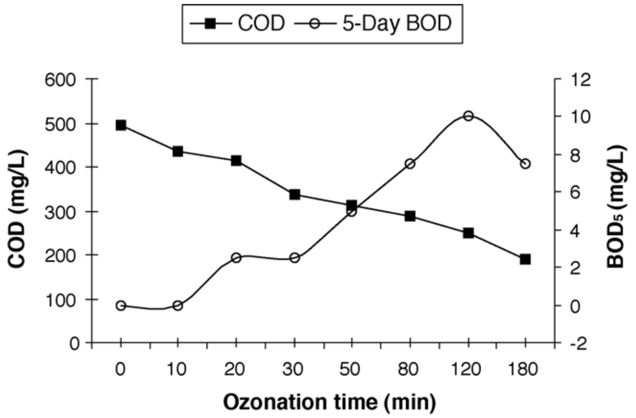

Fig. 5. COD and BOD_5 vs. ozonation time, at $C_{dye,i}$ = 500 mg/L.

decomposition of the generated products, therefore, the formation of more biodegradable secondary products is possible. In general, the change in biodegradability with ozonation is controlled by the ozonation rates of the initial dye compound and its primary oxidation products in competing reactions, which depend on the concentrations of these compounds and their resulting biodegradabilities [14].

In the literature, it was found that the maximum BOD_5/COD ratios varied between 0.27 and 0.56 for different substituted aromatics [14]. Also, maximum BOD_5/TOC ratio was 0.45, and for the same conditions, maximum BOD_5/COD ratio was 0.19 for 2,4-dinitrophenol [11]. In this study, maximum BOD_5/COD ratios of the ozonated Acid Red-151 solutions were found in the range of 0.028–0.35. From the results, at an initial Acid Red-151 concentration of 100 mg/L, the obtained maximum biodegradability ratio of 0.35 is a good value indicating biodegradability, when compared with the best BOD_5/COD ratios in the range of 0.4–0.5 reported in the literature [14].

3.3. Kinetic model [1,2]

A mathematical model was previously proposed by Liakou et al. [1], and some equations including the rates of dye elimination, the time rate of changes of COD, BOD_5 and the consumed ozone were given to determine the model parameters for Orange II. According to that model, the reactions taking place are assumed to be:

$$S_0 + \nu_1 O_{3\,(liq)} \rightarrow \nu_2 S_b + \nu_3 S_{nb} \tag{1}$$

$$S_b + \nu_4 O_{3\,(liq)} \rightarrow \nu_5 S_b + \nu_6 S_{nb} \tag{2}$$

$$S_{nb} + \nu_7 O_{3\,(liq)} \rightarrow \nu_8 S_b + \nu_9 S_{nb} \tag{3}$$

where S_0 expresses the dye concentration in equivalent COD units; S_b and S_{nb} express biodegradable and non-biodegradable compounds in equivalent COD units, respectively; ν_i values represent the stoichiometric coefficients. Also, the directly measurable quantities, namely the concentration of dye (C_A), COD and BOD_5 were correlated with S_0, S_b and S_{nb}, as follows:

$$C_A = aS_0 \tag{4}$$

$$\mathrm{COD} = S_0 + S_b + S_{nb} \tag{5}$$

$$\mathrm{BOD}_5 = bS_b \tag{6}$$

where the coefficient '*a*' is defined as moles of dye/equivalent COD in mg/L, and the coefficient '*b*' is defined as the BOD_5/COD ratio of the biodegradable compounds at each time.

The material balances in view of reactions (1)–(3) are:

$$\frac{dS_0}{dt} = -k_1 \cdot S_0 \cdot C_{O_3\,(liq)} \tag{7}$$

$$\frac{dS_b}{dt} = \nu_2 \cdot k_1 \cdot S_0 \cdot C_{O_3\,(liq)} + (\nu_5 - 1) \cdot k_2 \cdot S_b \cdot C_{O_3\,(liq)} + \nu_8 \cdot k_3 \cdot S_{nb} \cdot C_{O_3\,(liq)} \tag{8}$$

$$\frac{dS_{nb}}{dt} = \nu_3 \cdot k_1 \cdot S_0 \cdot C_{O_3\,(liq)} + \nu_6 \cdot k_2 \cdot S_b \cdot C_{O_3\,(liq)} + (\nu_9 - 1) \cdot k_3 \cdot S_{nb} \cdot C_{O_3\,(liq)} \tag{9}$$

$$\frac{dC_{O_3\,(liq)}}{dt} = \frac{q_g}{V_1} \cdot k_l a \cdot (C^0_{O_3\,(gas)} - H \cdot C_{O_3\,(liq)}) - \nu_1 \cdot k_1 \cdot S_0 \cdot C_{O_3\,(liq)} - \nu_4 \cdot k_2 \cdot S_b \cdot C_{O_3\,(liq)} - \nu_7 \cdot k_3 \cdot S_{nb} \cdot C_{O_3\,(liq)} \tag{10}$$

where k_i values are the rate constants. V_1, q_g, $k_l a$ are volume of reactor, flow rate of air, ozone mass transfer coefficient, respectively. Also, the first term on the right-hand side of Eq. (10) represents the rate of ozone transfer from gas to liquid phase. Liakou et al. [1] defined the function $F(t)$ as the total amount of ozone reacted with dye at time t:

$$F(t) = \int_0^t (\nu_1 \cdot k_1 \cdot S_0 \cdot C_{O_3\,(liq)} + \nu_4 \cdot k_2 \cdot S_b \cdot C_{O_3\,(liq)} + \nu_7 \cdot k_3 \cdot S_{nb} \cdot C_{O_3\,(liq)})\, dt \tag{11}$$

and

$$A(t) = \frac{dF(t)}{dt} \tag{12}$$

Due to the relations of (4)–(6) as well as definitions (11) and (12), the Eqs. (7)–(10) can be written as follows:

For dye:

$$\frac{dC_A}{dt} = -I_1 \cdot C_A \cdot C_{O_3\,(liq)} \tag{13}$$

For BOD_5:

$$\frac{d(\mathrm{BOD}_5)}{dt} = I_5 \cdot C_A \cdot C_{O_3\,(liq)} + I_6 \cdot (\mathrm{BOD}_5) \cdot C_{O_3\,(liq)} + I_7.(\mathrm{COD}) \cdot C_{O_3\,(liq)} \tag{14}$$

For COD:

$$\frac{d(\mathrm{COD})}{dt} = I_8 \cdot C_A \cdot C_{O_3\,(liq)} + I_9 \cdot (\mathrm{BOD}_5) \cdot C_{O_3\,(liq)} + I_{10} \cdot (\mathrm{COD}) \cdot C_{O_3\,(liq)} \tag{15}$$

For residual ozone concentration in liquid phase:

$$\frac{dC_{O_3\,(liq)}}{dt} = \frac{q_g}{V_1} \cdot k_l a \cdot (C^0_{O_3\,(gas)} - H \cdot C_{O_3\,(liq)}) - I_2 \cdot C_A \cdot C_{O_3\,(liq)} - I_3(\mathrm{BOD}_5) \cdot C_{O_3\,(liq)} - I_4 \cdot (\mathrm{COD}) \cdot C_{O_3\,(liq)} \tag{16}$$

where I_i are the parameters of the model derived from the combinations of Eqs. (4)–(12) which are directly related to the stoichiometric coefficients ν_i, the kinetic rate constants k_i, and the conversion factors '*a*' and '*b*' which change with time.

The present data of dye concentration, BOD_5, COD and the amount of dissolved (residual) ozone at different ozonation times

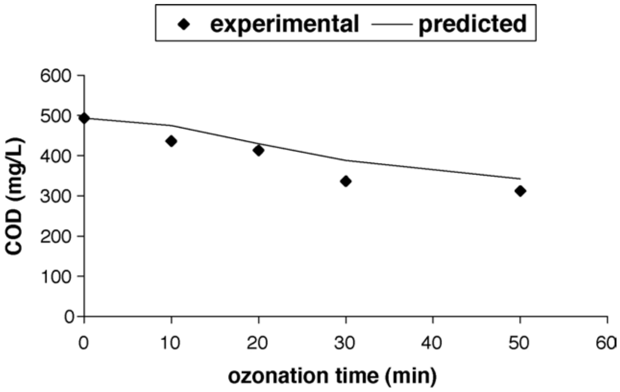

Fig. 6. Experimental and model predicted profiles of COD for $C_{\mathrm{dye,i}} = 500$ mg/L.

of Acid Red-151 are used in these equations. These data versus ozonation time are drawn for each initial dye concentration and the curves are fitted to the data, thus the obtained polynomial equations are given elsewhere [15]. The model equations are written at specific times; the derivative parts of the equations are obtained by differentiating these polynomials and calculating their values at each specific time value, and the right-hand sides of the equations are evaluated from the experimental data. Finally, three sets of equations with three unknowns are obtained to be further solved by *Mathematica* for the model parameters: I_1 to I_{10} and $k_{\mathrm{l}}a$.

This model is expressed directly in terms of readily measurable quantities. The values of the model parameters estimated from the experimental data using least squares method in the units of L/(mg min) are:

$$I_1 = 444.75 \times 10^{-3};\ I_2 = -8.879 \times 10^{-3};$$

$$I_3 = -2.793 \times 10^{-3};\ I_4 = -0.0413 \times 10^{-3};$$

$$I_5 = 24.840 \times 10^{-3};\ I_6 = -50.420 \times 10^{-3};$$

$$I_7 = -5.790 \times 10^{-3};\ I_8 = -30.7 \times 10^{-3};$$

$$I_9 = 331.9\times10^{-3};\ I_{10} = -84.94\times10^{-3};\ k_{\mathrm{l}}a = 1.2035\times10^{-3}.$$

After finding the model parameters, the predicted curves of the model are drawn by evaluating the numerical integrations on the right-hand sides of Eqs. (13)–(16) for different time intervals starting from $t = 0$ by using a Fortran program [15]. The predicted profiles of COD, dye (Acid Red-151) concentration, and dissolved ozone concentration in the liquid phase are given in Figs. 6–8 for $C_{\mathrm{dye,i}} = 500$ mg/L. As observed in these figures, the model gives a satisfactory fit to the experimental data.

The positive or negative signs of the estimated parameters may be due to the occurrence of some error in the least squares fit to very small concentrations measured. Actually, hereby-reported model parameters are the chosen average values from the whole predicted results at different initial dye concentrations, given in Table 1 to clarify the arised questions about the reliability of the results. Nevertheless, they have reasonable physical significance with respect to the rate constants and stoichiometric coefficients according to the corresponding equalities given below:

$$I_1 = k_1;\ I_2 = \nu_1 k_1;\ I_3 = \nu_4 k_2;\ I_4 = \nu_7 k_3;\ I_5 = \nu_2 k_1;$$

$$I_6 = (\nu_5 - 1)k_2;\ I_7 = \nu_8 k_3;\ I_8 = \nu_3 k_1;$$

$$I_9 = \nu_6 k_2;\ I_{10} = (\nu_9 - 1)k_3.$$

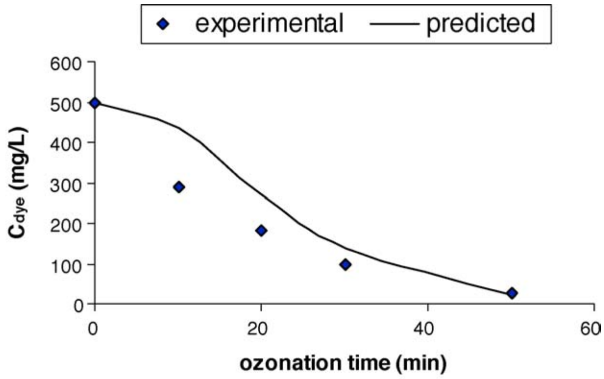

Fig. 7. Experimental and model predicted profiles of C_{dye} for $C_{\mathrm{dye,i}} = 500$ mg/L.

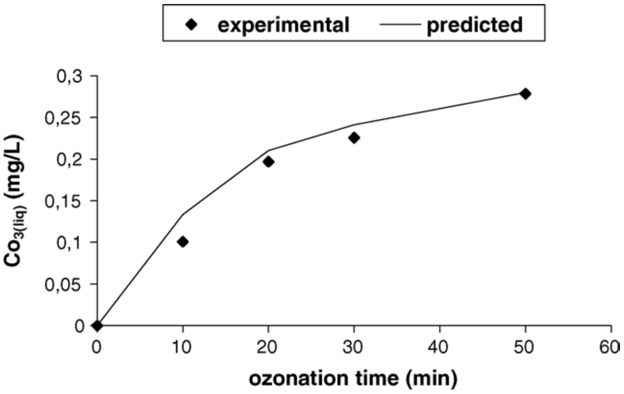

Fig. 8. Experimental and model predicted profiles of $C_{\mathrm{O}_{3\,(\mathrm{liq})}}$ for $C_{\mathrm{dye,i}} = 500$ mg/L.

Also Liakou et al. [1] obtained some of these parameters as negative or positive in their fit by least squares method, but still they related them to the rate constants and stoichiometric coefficients in the proposed reactions to some degree. In the

Table 1
Predicted model parameters for the continuous ozonation of Acid Red-151

Model parameters (L/(mg min))	$C_{\mathrm{dye,i}}$ (mg/L)			
	100	250	500	1000
I_1	0.4795	1.027	0.38	0.11579
I_2	0.00555	−0.04067	−0.00025	−0.000145
I_3	0.001327	−0.00704	−0.0065	0.00104
I_4	−0.000183	0.000068	0.00028	−0.00033
I_5	−0.0674	0.02242	0.02484	0.02711
I_6	−0.2857	−0.3991	−0.00191	0.21049
I_7	0.04367	0.00848	−0.00579	−0.00606
I_8	−0.24	0.9113	−0.0307	−0.11598
I_9	1.0685	−1.9318	3.3116	−1.12074
I_{10}	−0.1147	−0.1708	−0.0623	0.00804
$k_{\mathrm{l}}a$	0.001667	–	0.00074	–

second part of their work [2], they also considered the individual ozonation of intermediate products from the oxidation of Orange II by ozone, which were formic acid, oxalic acid and benzenesulfonate. By the ozonation of formic acid only, they determined the rate constant k_1 independently and reported as 319.13 L/(g min). In this work, although the type of azo dye is different, it can be said that the same intermediate products probably result from the oxidation of Acid Red-151, which has a very similar structure to Orange II, and the average value of I_1 corresponding to k_1 is obtained as 444.75 L/(g min). This value is in the same order of magnitude with their finding. Besides, the average stoichiometric constant ν_2 is found equal to 0.0558 in this work, which is equal to the conversion ratio of COD to BOD_5, namely 'b'. This shows that some non-biodegradables are converted to biodegradable products with this stoichiometric coefficient which is logical. The stoichiometric constant ν_3 is found as negative as a result of the negatively obtained model parameter I_3 suggesting that in reaction (1), S_{nb} is not a product but a reactant. That is some nonbiodegradable chemicals in the medium are oxidized by ozone too, such as the chemicals used to adjust the pH to the desired value in the reaction medium. The reason for obtaining the model parameters of I_2, I_3 and I_4 as negatives may be due to the error in the least squares fit as seen in Table 1; because, these were obtained as positive values at some initial dye concentrations. The reason for obtaining I_6 and I_{10} as negatives may be due to their values being less than 1, although this is not possible to claim here, since the reaction rate constants k_2 and k_3 have not been determined independently in this study. It can be concluded that the fit of the present experimental data to the proposed model can still be considered satisfactory to yield these results. Because, the k_la value obtained in this work also is in good agreement with the literature value. Liakou et al. [1,2] obtained this value as 0.707 in the ozonation of intermediate product, formic acid, and as 2.97 in the ozonation of Orange II, when the ozone production rate is 7.1 mg/(L min) in a reactor of 0.5 L volume with constant stirring, while it is obtained here in the range of 0.74–1.67 (as average value of 1.2), when the ozone production rate is 0.282 mg/(L min) in a reactor of 1 L volume with constant stirring, The present result is in the same order of magnitude with the previous ones [1,2].

Here, it must also be noted that the Henry's constant is taken as H = 4570 atm at 25 °C, and then it is converted to the required units of Eq. (16), the result being $H = 3.362$ (L.liq./L.gas). The details of the unit conversion is given elsewhere [15].

4. Conclusions

This work verifies that ozonation is capable of a rapid conversion of the Acid Red-151 dye molecule to more biodegradable intermediates up to the ozonation time of 120 min at which the optimum BOD_5/COD ratio is obtained, as the same type of behaviour observed by Liakou et al. [1,2] for Orange II, another azo dye. The peak BOD_5/COD ratios were found to be in the range of 0.028–0.35 for the initial dye concentrations being in the range of 1000–100 mg/L, respectively. The proposed kinetic modeling by Liakou et al. [1,2] could be satisfactorily applied to the continuous ozonation of Acid Red-151, which allowed the prediction of the key variables measured experimentally, regardless of the particular intermediate compounds generated during ozonation. The model parameters were estimated using the least squares method to fit the present experimental data to this model which yielded a very good fit.

References

[1] S. Liakou, S. Pavlou, G. Lyberatos, Ozonation of azo dyes, Water Sci. Technol. 35 (4) (1997) 279–286.

[2] S. Liakou, M. Kornaros, G. Lyberatos, Pretreatment of azo dyes using ozone, Water Sci. Technol. 36 (2–3) (1997) 155–163.

[3] S.H. Lin, C.M. Lin, Treatment of textile waste effluents by ozonation and chemical coagulation, Water Res. 27 (1993) 1743–1748.

[4] I. Arslan, A.I. Balcıoğlu, Advanced oxidation of raw and biotreated textile industry wastewater with O_3, H_2O_2/UV-C and their sequential application, J. Chem. Technol. Biotechnol. 76 (2001) 53–60.

[5] L. Calvosa, A. Monteverdi, B. Rindone, G. Riva, Ozone oxidation of compounds resistant to biological degradation, Water Res. 25 (1991) 985–993.

[6] J.M. Green, C. Sokol, Using ozone to decolorize dyeing plant wastewater, Am. Dystuff Rep. 74 (1985) 50–67.

[7] F. Erol, A Kinetic Study on the Decolorization of Aqueous Solutions of Acid Red-151 by Ozonation, M.S. Thesis, Department of Chemical Engineering, Middle East Technical University, Ankara, Turkey, 2002.

[8] T.A. Ozbelge, F. Erol, H.O. Ozbelge, A kinetic study on the decolorization of aqueous solutions of Acid Red-151 by ozonation, J. Environ. Eng. Sci. Health: Part A 38 (8) (2003) 1607–1623.

[9] APHA, Standard Methods for the Examination of Water and Wastewater, 18th ed., APHA, Washington, DC, USA, 1992.

[10] H. Bader, J. Hoigne, Determination of ozone in water by indigo method, Water Res. 15 (1981) 449–456.

[11] D.R. Medley, E.L. Stover, Effects of ozone on the biodegradability of biorefractory pollutants, J. WPCF 55 (1983) 489–494.

[12] N. Takahashi, T. Nakai, Y. Satoh, Y. Katoh, Variation of biodegradability of nitrogenous organic compounds by ozonation, Water Res. 28 (1994) 1563–1570.

[13] F.J. Beltran, J.F. Garcia-Araya, P.M. Alvarez, Integration of continuous biological and chemical (ozone) treatment of domestic wastewater: 1. Biodegradation and post-ozonation, J. Chem. Technol. Biotechnol. 74 (1999) 877–883.

[14] E. Gilbert, Biodegradability of ozonation products as a function of COD and DOC elimination by example of substituted aromatic substances, Water Res. 21 (1987) 1273–1278.

[15] F. Gokcen, Treatment of an Azo Dye by Combined Ozonation and Once-Thro Activated Sludge Process. M.S. Thesis, Department of Chemical Engineering, Middle East Technical University, Ankara, Turkey, 2003.