



## Detection of double bond-ozone stoichiometry by an iodimetric method during ozonation processes

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### ABSTRACT

In this study, the stoichiometry of decolorization of four dyes (*Basic Yellow 28*, *Malachite Green*, *Reactive Black 5* and *Reactive Red 198*) was investigated using ozonation processes. The decolorization of *Basic Yellow 28* (BY28) and *Malachite Green* (MG) was optimal at an acidic pH value of 3, whereas decolorization of *Reactive Black 5* (RB5) and *Reactive Red 198* (RR198) was optimal at a basic pH of 10. Stoichiometric Ratios (SR) between ozone and dyes were calculated to be 3.5, 7.1, 11 and 16.1 for BY28, MG, RB5 and RR198, respectively. The correlation between ozone-double bond (DB) with the best linear fit and the least relative error ( $\varepsilon$  (%)) was between aromatic ring number ( $A_n^R$ ) and SR, with regression coefficients of 0.993 and 4.6, respectively. Also, the relationship between total double bond number ( $DBN_T$ )–SR had respective values of 5.1 and 0.983 for the  $\varepsilon$  (%) and regression coefficient. Additionally, the pseudo-first order decolorization rate constants,  $k'$ , were decreased from aromatic ring number 2 ( $A_2^R$ ) to aromatic ring number 5 ( $A_5^R$ ).

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### 1. Introduction

Recently, decolorization of dyes has been studied extensively because of their significant contribution to environmental pollution [1–4]. In the past year, 29.4 million tons of dye were produced worldwide [5,6]. Dyes are used in the textile, leather, pharmaceutical, printing, plastic, cosmetics, and food industries [7,8]. Because most dyes are toxic and potentially carcinogenic, the large volumes of wastewater and contaminants generated by factories threaten human health [9]. Furthermore, colored wastewater affects the aesthetic merit and water transparency of receiving waterbodies [10,11]. Many different types of dyes exist from a variety of classes, including azo, anthraquinone, phthalocyanine, direct, reactive, dispersive, acidic, basic, and neutral classes. Even at low concentrations, dyes with azo, anthraquinone, and phthalocyanin as defined chromophoric systems give color to water. Solar irradiation can be absorbed by these systems, and solar irradiation intensity is vitally important for photosynthetic activity. However, in deep water, solar irradiation may not reach the bottom or its intensity will be very low.

Conventional wastewater treatment methods, such as biological processing, coagulation, and flocculation, are successful for color removal, but they also cause new problems. Excess sludge production due to pollution is not degraded and only changes phase from wastewater to biomass or sludge. In recent years, advanced oxidation processes (AOPs) have been used as an alternative technology based on the degradation of organic pollutants, ozonolysis [12], and Fenton [13], photocatalytic [14,15], and wet-air oxidation [1,2]. Among the AOPs, treatment with ozone processes has yielded the most favorable results [13]. Most studies have focused on discolorization, degradation mechanisms, and mineralization reactions in dye-ozone reactions [16–18], and few have reported the relationship between ozone-substrate and the stoichiometry of the degradation reaction during ozonation processes [19,20].

Ozonolysis, the reaction of ozone with a carbon-carbon double bond (C=C), is well known. The C=C bonds are very attractive centers for addition reactions by ozone to yield unstable intermediates, known as ozonides. According to the resonance hybrid structure of ozone, it can behave either as an electrophilic or nucleophilic reagent in its initial attack [21]. There is a greater possibility of electrophilic attack than nucleophilic attack in the ozonolysis of carbon-carbon unsaturated bonds; however, electrophilic attacks are more common toward carbon-nitrogen double bonds [22,23]. Despite the mechanism, a stoichiomet-

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ric relationship must exist between ozone and the double bond.

Textile dyes are composed of C=C, C=N, and N=N double bonds. Generally, these double bonds are established in aromatic rings and create conjugation systems throughout dye molecules, making them ideal subjects for stoichiometric studies.

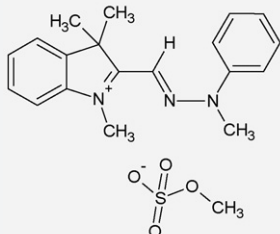
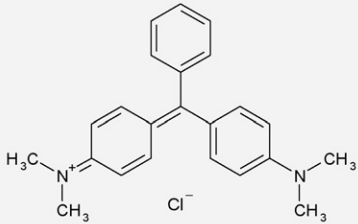
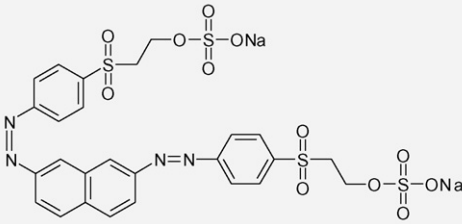
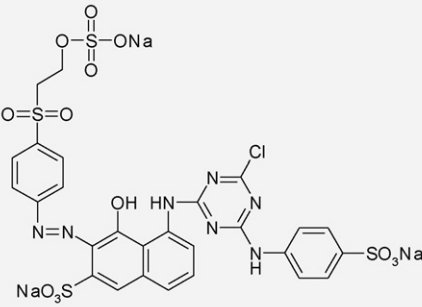
The iodimetric method has been used for the determination of ozone concentration in solution by many researchers [24,25]. Iodimetry, with a detection limit of  $0.1 \text{ mg dm}^{-3}$ , is fairly inexpensive, easily applicable, and has good repeatability (2%). The limit

of detection can be reduced to  $0.01 \text{ mg dm}^{-3}$  by adding moderate thiosulfate concentrations, as nitrogen oxide and other oxidants of iodide ion can interfere if present. For discolorization studies, there is a very low possibility that these oxides are present and that the mineralization reaction will not be completed [7,26,27].

The first aim of this study was to determine the stoichiometric ratio between ozone and double bonds for dyes composed of 2, 3, 4, and 5 aromatic rings in water until discolorization by ozonolytic processes. The second aim was to characterize the kinetics of discolorization.

**Table 1**

Chemical structure and characterization of dyes.

Dyes	$\lambda_{\text{max}}$ (nm)	Chemical formula
Basic Yellow 28  C.I. Basic Yellow 28 C.I. No. 48054 MW: $433.52 \text{ g mol}^{-1}$	438	
Malachite Green  C.I.: Basic Green 4 C.I. No. 42000 MW: $364.91 \text{ g mol}^{-1}$	618	
Reactive Black 5  C.I. Reactive Black 5 C.I. No. 20505 MW: $991.82 \text{ g mol}^{-1}$	580	
Reactive Red 198  C.I. Reactive Red 198 C.I. No. - MW: $968.21 \text{ g mol}^{-1}$	542	

## 2. Materials and methods

### 2.1. Materials

MG dye (for stoichiometric experiments only) was purchased from Riedel-de Haen AG (96%, Germany) and used without further purification. BY28 (97%), RB5 (100%), and RR198 (98%) were supplied from Dye Star (Table 1). Ozone gas was produced from pure oxygen (99.99%) by an Ozo-1VTT model ozone generator (Ozomax, Canada). The gas flow rate was monitored by a flow meter on the oxygen gas tube. Other chemicals were purchased from Merck (Germany).

### 2.2. Ozonolysis experiments

Necessary pH adjustments were made by titrating 0.1 mol dm<sup>-3</sup> orthophosphoric acid with sodium hydroxide, and buffered solutions of dyes were prepared at different initial concentrations (0.3035–1.8211 mmol dm<sup>-3</sup>) for each dye. 500 cm<sup>3</sup> of the dye solution was placed into a 1000 cm<sup>3</sup> reaction tube (Pyrex), and the ozone gas was diffused into the reaction mixture through a glass sparger at the bottom of the reactor. 1 cm<sup>3</sup> samples were taken every 2 min for 30 min, with a dye concentration of 0.9106 mmol dm<sup>-3</sup> at pH 3, 7 and 10.

Kinetic experiments were carried out at six dye concentrations ranging from 0.3035 to 1.8211 mmol dm<sup>-3</sup> in a buffer of pH 3 at a constant temperature of 19 °C and constant O<sub>2</sub> gas inlet velocity. 1 cm<sup>3</sup> samples were taken every 2 min for 30 min for BY28, RB5 and RR198, and the dye solution absorbance was analyzed using a Shimadzu UV-1800 PC scanning spectrophotometer at 438, 580 and 542 nm, respectively.

Ozone traps containing 500 cm<sup>3</sup> of potassium iodide solution (KI) (20 g dm<sup>-3</sup>) were used, with the outlet of the reaction mixture tube set to measure the excess ozone concentration produced. The trap contents were titrated with standardized sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) (0.0100 mol dm<sup>-3</sup>), and ozone concentrations were determined by the amount of titrant volume [28]. To determine the total ozone concentration diffused in the reaction mixture at constant O<sub>2</sub> gas inlet velocity, 500 cm<sup>3</sup> of KI solution (pH 3) was added to the reaction tube. The KI trap and reaction tube were titrated again with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> at the end of the experiment. The amount of consumed ozone (in mmol) by dyes was calculated for each initial dye concentration according to (Eq. (1)):

$$O_3^{\text{Consumed}} = O_3^{\text{Total}} - O_3^{\text{Trap}} \quad (1)$$

where  $O_3^{\text{Consumed}}$  is the amount of ozone (in mmol) reacted with dye molecules,  $O_3^{\text{Total}}$  is the total amount of ozone (in mmol) produced by the ozone generator in an experiment, and  $O_3^{\text{Trap}}$  is the excess ozone captured by the KI trap.

To determine the ozone solubility in a buffer at pH 3, ionic strength of 0.12 mol dm<sup>-3</sup>, 500 cm<sup>3</sup> of the buffer solution was placed in the reaction tube, and ozone gas was diffused for 10 min. After this time, 200 cm<sup>3</sup> of this solution was placed in a 1000 cm<sup>3</sup> Erlenmeyer flask, and 200 cm<sup>3</sup> KI solution (20 g dm<sup>-3</sup>) was added. The mixture was shaken vigorously in the dark and then titrated with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The solubility of ozone was determined as 6.54 mg dm<sup>-3</sup>. In addition to, according to the Debye–Hückel theory, the solubility of ozone was calculated theoretically as 6.46 mg dm<sup>-3</sup> at 0.12 mol dm<sup>-3</sup> ionic strength [29].

## 3. Results and discussion

### 3.1. The effect of pH on ozonolytic degradation of BY28, RB5 and RR198

The experiments were carried out with a 0.9106 mmol dm<sup>-3</sup> dye concentration at pH values of 3, 7 and 10 (Fig. 1). The amount of decomposed dyes was under the 5% level at pH 3, 7, 10 and 10 for the first 30 min of ozonolysis time for BY28, MG, RB5 and RR198, respectively. Ozone reacts with organic compounds in two different ways depending on the pH. One is by direct attack at acidic pH values and the other is by free radical attack at basic pH values [17]. The decomposition reaction between molecular ozone and BY28 was more selective than that of radicals, especially hydroxyl radicals, while RB5 and RR198 exhibited opposite selectivity. Decolorization of BY28 was obtained for 98.5% and 82% of the 0.9106 mmol dm<sup>-3</sup> dye concentration at 7 min of ozonation time for pH 3 and pH 10, respectively. The attack of ozone to BY28 was 15% more effective than that of the hydroxyl radical, although its oxidation potential (2.8 V) is higher than ozone. As shown in Figs. 2 and 3, decolorization of RB5 and RR198 was higher at basic pH values; the respective decomposition of these dyes was 100% and 96%. The differences of the decomposition of dyes between these pH values were calculated as 11% and 37% for RB5 and RR198, respectively.

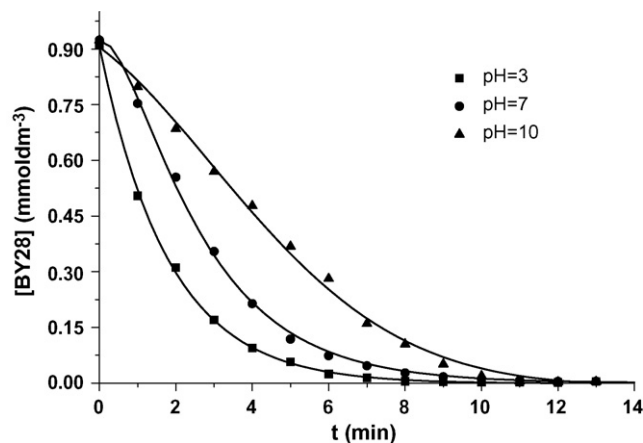


Fig. 1. Ozonolytic degradation of BY28 at various pH values ( $[BY28]_0 = 0.9106 \text{ mmol dm}^{-3}$ ).

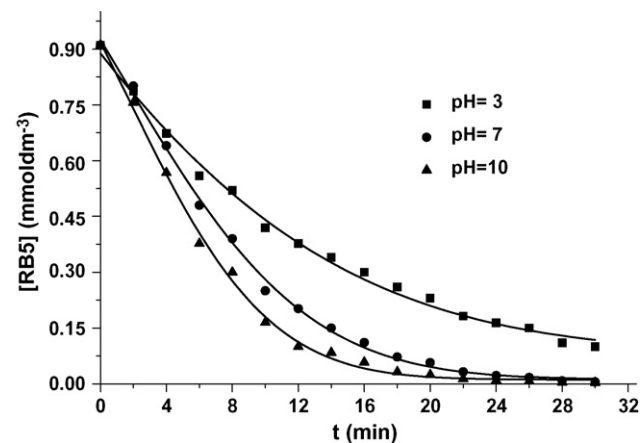


Fig. 2. Ozonolytic degradation of RB5 at various pH values ( $[RB5]_0 = 0.9106 \text{ mmol dm}^{-3}$ ).

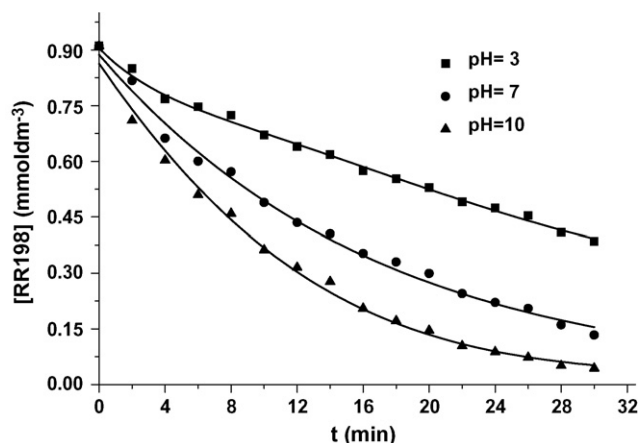


Fig. 3. Ozonolytic degradation of RR198 at various pH values ( $[RR198]_0 = 0.9106 \text{ mmol dm}^{-3}$ ).

### 3.2. Stoichiometric ratio between ozone and dyes

The stoichiometric ratio of the ozone-dye decolorization reactions was determined for each initial dye concentration and is reported in Table 2 and Fig. 4. When the ratio of the decolorization of dyes reached over 95%, the reaction was stopped, and the ozone consumption was calculated by titration with  $0.010 \text{ mol dm}^{-3} \text{ Na}_2\text{S}_2\text{O}_3$ . The longest ozone consumption time, 50 min, was carried out by RR198. Eighty-two percent of the  $17.50 \text{ mmol}$  ozone produced by the ozone generator was consumed by RR198. The second longest time was for the ozone-RB5 decolorization reaction. In this reaction, which was 38 min long, ozone consumption was 81% of the  $13.30 \text{ mmol}$  of ozone produced. The ozone consumption of MG and BY28 was  $6.33$  and  $3.20 \text{ mmol}$  for ozonation times of 16 min and 10 min, respectively.

The ozone consumption was proportionally linear to the initial dye concentrations (Fig. 4). According to Fig. 4, the stoichiometric ratio ( $n_{\text{O}_3}/n_{\text{dye}}$ ) was calculated to be approximately 3.5, 7.1, 11.0

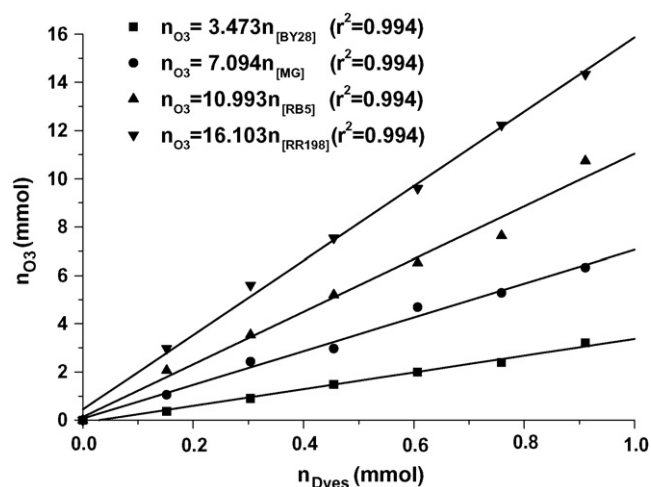


Fig. 4. Stoichiometric relationship between ozone and dye concentrations.

and 16.1 for the decolorization reaction with regression coefficients of 0.994 for BY28, MG, RB5 and RR198, respectively.

The reaction between molecular ozone and carbon-carbon double bonds (DB) is well known. The mechanism of ozone addition to alkenes begins with the formation of unstable compounds called initial ozonides. The process occurs vigorously and leads to the spontaneous rearrangement to compounds known as ozonides. Ozonides are very unstable compounds that are degraded to aldehydes or ketones [30]. The DBs of dyes with potential for cleavage with ozone and their stoichiometric ratios are shown for each dye in Table 3. The relationships between the stoichiometric ratios for each dye and the total double bond number ( $DBN_T$ ), total C=C double bond number ( $DBN_{C=C}$ ),  $A_N^R$ , and C=C + C=N double bond number (except N=N double bonds,  $DBN_{N=N}$ ) in the decolorization reactions are shown in Fig. 5. While it was thought that ozone only reacted with C=C double bonds, the regression coefficient (0.801) between  $DBN_{C=C}$  and stoichiometric ratios was very low. Similarly,

Table 2

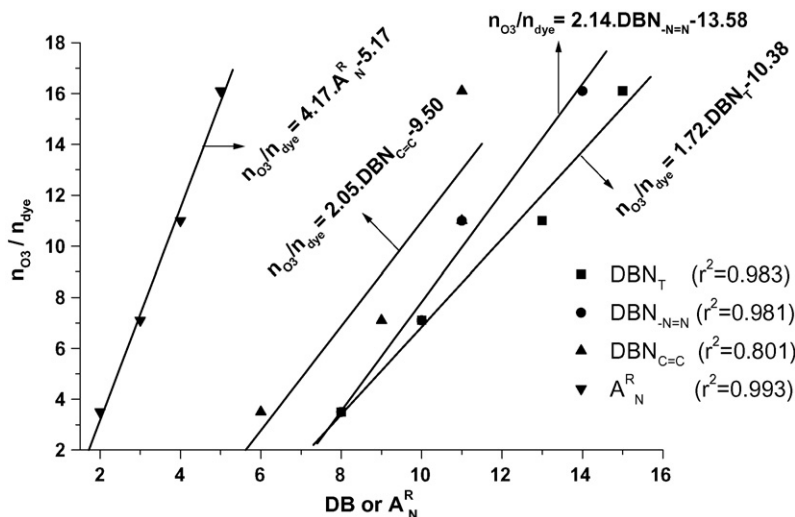
Determination of consumed ozone by dye molecules during ozonolysis experiments at different initial dye concentrations for each dye, titrated volume of KI trap contents, and titrant volume.

Dyes	Produced O <sub>3</sub> (mmol)	Initial dyes (mmol)	Volume, cm <sup>3</sup> (trap content)	Titratant <sup>a</sup> vol. cm <sup>3</sup> 0.010 mol dm <sup>-3</sup> Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	Excess O <sub>3</sub> in trap (mmol)	Consumed O <sub>3</sub> by dye (mmol)
BY28	3.5	0.911	200	60	0.30	3.20
		0.759	100	220	1.10	2.40
		0.607	100	300	1.50	2.00
		0.455	50	402	2.01	1.49
		0.304	50	520	2.60	0.90
		0.152	50	626	3.13	0.37
MG	7.0	0.911	200	134	0.67	6.33
		0.759	100	344	1.72	5.28
		0.607	50	462	2.31	4.69
		0.455	25	806	4.03	2.97
		0.304	25	914	4.57	2.43
		0.152	25	1190	5.95	1.05
RB5	13.3	0.911	25	512	2.56	10.74
		0.759	25	1132	5.66	7.64
		0.607	25	1356	6.78	6.52
		0.455	20	1620	8.10	5.20
		0.304	10	1952	9.76	3.54
		0.152	10	2248	11.24	2.06
RR198	17.5	0.911	25	632	3.16	14.34
		0.759	25	1054	5.27	12.23
		0.607	20	1580	7.90	9.60
		0.455	10	1992	9.96	7.54
		0.304	10	2380	11.90	5.60
		0.152	10	2906	14.53	2.97

<sup>a</sup> The trap contents titrated by  $0.010 \text{ mol dm}^{-3} \text{ Na}_2\text{S}_2\text{O}_3$  were normalized to a reaction volume of  $500 \text{ cm}^3$ .

**Table 3**  
Stoichiometric ratios and characteristic double bond numbers of each dye.

Dyes	DBN <sub>T</sub> (C=C,N=N,C=N)	DBN <sub>-N=N</sub> (Except N=N)	DBN <sub>C=C</sub> (C=C)	A <sub>N</sub> <sup>R</sup>	n <sub>O<sub>3</sub></sub> /n <sub>dye</sub>
BY28	8	8	6	2	3.5
MG	10	10	9	3	7.1
RB5	13	11	11	4	11.0
RR198	15	14	11	5	16.1



**Fig. 5.** Linear fit of stoichiometric ratios as a function of characteristic double bond numbers and A<sub>N</sub><sup>R</sup> for each dye.

the relevant value for DBN<sub>-N=N</sub> included C=N double bond number on DBN<sub>C=C</sub>, was observed higher than DBN<sub>C=C</sub> 0.981. The respective regression coefficients were calculated as 0.983 and 0.993 from the slopes of the plots of stoichiometric ratio versus DBN<sub>T</sub> and A<sub>N</sub><sup>R</sup>.

In this study, the average percentage errors between the experimental and predicted values were calculated using Eq. (2).

$$\varepsilon (\%) = \frac{\sum_i^N |[(SR_i)_{cal} - (SR_i)_{exp}] / (SR_i)_{exp}|}{N} \times 100 \quad (2)$$

where  $\varepsilon$  (%) is the average percentage error, SR is the stoichiometric ratio, n<sub>O<sub>3</sub></sub>/n<sub>Dye</sub>, with the experimental and calculated values of SR indicated by exp and cal, N is the number of measurements.

Table 4 shows the average percentage errors between the experimental and calculated data. According to these results, the highest value for  $\varepsilon$  (%) of SR calculated by using the equation for the stoichiometric ratio derived from the DBN<sub>C=C</sub> function,

SR = 2.05DBN<sub>C=C</sub> – 9.50, was 60.7. The second highest value of  $\varepsilon$  (%), 14.9, was calculated the same way for SR = 2.14DBN<sub>-N=N</sub>–13.58. For both DBN<sub>T</sub> and A<sub>N</sub><sup>R</sup>, the relevant values were less than 10, with values of 5.1 and 4.6 for the DBN<sub>T</sub> and A<sub>N</sub><sup>R</sup> functions, respectively. Although double bonds out of aromatic rings (two C=N in BY28, one C=N in MG, two N=N in RB5, and one N=N in RR198) were not included in A<sub>N</sub><sup>R</sup>, both the observed regression coefficient and  $\varepsilon$  (%) were better values when compared with the others. Therefore, it can be concluded that ozone reacted selectively with A<sub>N</sub><sup>R</sup> in dye molecules via molecular addition to double bonds at acidic pH values or by a free radical mechanism at basic pH values.

### 3.3. Ozonolytic degradation and kinetics of dyes

The degradation experiments of BY28, RB5 and RR198 were carried out with initial concentrations of 0.3035, 0.6071, 0.9106,

**Table 4**  
The average percentage errors of derived equations depend on the characteristic double bond numbers of each dye.

Double bonds characteristics	Equations	Dyes	n <sub>O<sub>3</sub></sub> /n <sub>Dye</sub> Calculated values	$\varepsilon$ (%)
DBN <sub>T</sub> (C=C,N=N,C=N)	SR = 1.72 DBN <sub>T</sub> –10.38	BY28	3.4	5.1
		MG	6.8	
		RB5	12.0	
		RR198	15.4	
DBN <sub>-N=N</sub> (C=C,C=N)	SR = 2.14.DBN <sub>-N=N</sub> –13.58	BY28	3.6	14.9
		MG	7.9	
		RB5	14.3	
		RR198	18.6	
DBN <sub>C=C</sub>	SR = 2.05.DBN <sub>C=C</sub> – 9.50	BY28	6.9	60.7
		MG	11.0	
		RB5	17.5	
		RR198	21.2	
A <sub>N</sub> <sup>R</sup>	SR = 4.17 A <sub>N</sub> <sup>R</sup> – 5.17	BY28	3.2	4.6
		MG	7.3	
		RB5	11.5	
		RR198	15.7	



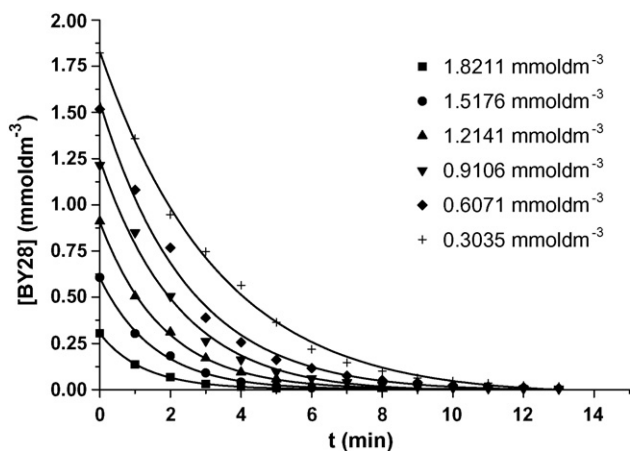


Fig. 6. Degradation of BY28 in solutions of various initial concentrations by ozonation application (pH 3).

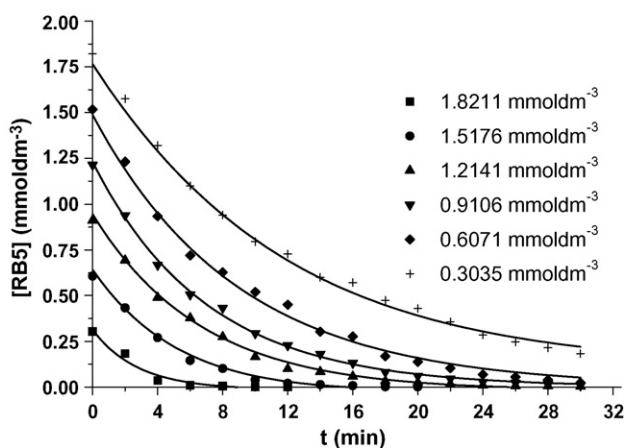


Fig. 7. Degradation of RB5 in solutions of various initial concentrations by ozonation application (pH 3).

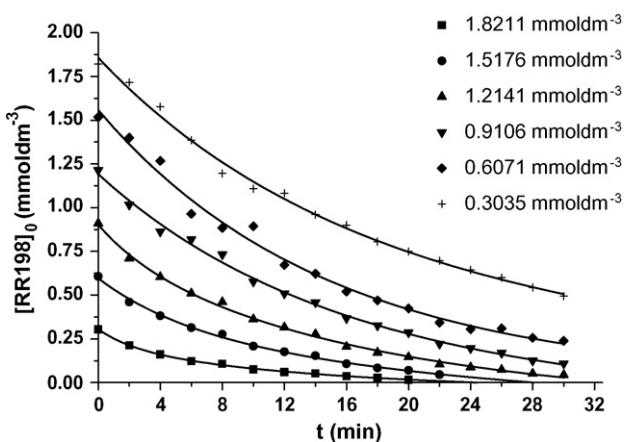


Fig. 8. Degradation of RR198 in solutions of various initial concentrations by ozonation application (pH 3).

1.2141, 1.5176 and 1.8211 mmoldm<sup>-3</sup> dye at pH 3, pH 10 and pH 10 for BY28, RB5 and RR198, respectively. Figs. 6–8 show the decolorization of BY28, RB5 and RR198 at different initial dye concentrations with varying ozonation times. The more diluted the initial solution, the faster the degradation occurred. For instance, BY28, at an initial concentration of 0.3035 mmoldm<sup>-3</sup>, was degraded completely after a reaction time of 4 min while it,

Table 5

*k'* rate constants, half-lives and initial degradation rates of BY28, RB5 and RR198.

Dyes	[Dye] <sub>0</sub> (mmoldm <sup>-3</sup> )	<i>k'</i> (s <sup>-1</sup> )	<i>t</i> <sub>1/2</sub> (s)
BY28	1.8211	0.0060	114
	1.5176	0.0069	102
	1.2141	0.0080	90
	0.9106	0.0101	66
	0.6071	0.0114	60
	0.3035	0.0127	54
RB5	1.8211	0.0013	546
	1.5176	0.0021	330
	1.2141	0.0026	270
	0.9106	0.0039	180
	0.6071	0.0050	138
	0.3035	0.0062	114
RR198	1.8211	0.0007	948
	1.5176	0.0011	648
	1.2141	0.0013	480
	0.9106	0.0016	426
	0.6071	0.0018	384
	0.3035	0.0023	300

at 1.8211 mmoldm<sup>-3</sup> initial concentration, was degraded about to 69% of dye.

The decolorization times of dyes were inversely proportional with  $A_N^R$  during the ozonation processes. With an initial concentration of 1.8211 mmoldm<sup>-3</sup> BY28, the degradation,  $A_2^R$ , was complete in an ozonation time of 12 min, whereas the degradation of RB5,  $A_4^R$  and RR198,  $A_5^R$ , was 60% and 40.5% complete.

The kinetics of the dyes were analyzed using the kinetic equation,  $-d[\text{Dye}]/dt = k'[\text{Dye}]$ . Pseudo-first order rate constants for each compound were calculated from the slope of the plot of  $-\ln([\text{Dye}]/[\text{Dye}]_0)$  versus time.

An inverse relationship was revealed between the initial dye concentration and the pseudo-first order kinetic rate constants (Table 5). For initial dye concentrations of 1.8211–0.3035 mmoldm<sup>-3</sup>, the respective first order rate constants were in the range of 0.0060–0.0127 s<sup>-1</sup>, 0.0013–0.0062 s<sup>-1</sup> and 0.0007–0.0023 s<sup>-1</sup> for BY28, RB5 and RR198.

#### 4. Conclusion

In this work, the optimum decolorization pH values by ozonation processes were determined for each dye to be acidic (pH 3) for BY28 and MG and basic (pH 10) for RB5 and RR198 because of their effective mechanisms of decolorization. At the acidic pH, ozone can directly react with BY28 and MG as an electrophile, while at the basic pH, ozone reacts radically with RB5 and RR198. Whether the ozone addition to the double bond occurs molecularly or radically, the amount of ozone consumed by the double bond was constant. The plot of SR versus DBs was strongly linear. The determination of SR between ozone and dye molecules (BY28, MG, RB5 and RR198) in decolorization experiments was achieved even  $2.1 \times 10^{-4}$  mmol O<sub>3</sub> dm<sup>-3</sup> level by using iodometric method. SRs between ozone and dyes were calculated to be 3.5, 7.1, 11 and 16.1 for BY28, MG, RB5 and RR198, respectively. The consumed ozone by double bonds was enhanced by increasing the double bond number. The  $A_N^R$  and  $DBN_T$  of dyes were noted to be linearly proportional with ozone consumption. The relationship between ozone–DB was strongest between  $A_N^R$  and SR, with a regression coefficient of 0.993. Also, the SR– $DBN_T$  relationship exhibited a similar behavior, with a value of 0.983 for the regression coefficient.  $\varepsilon$  (%) of equations obtained were also calculated. The smallest value of  $\varepsilon$  (%), 4.6, was observed for ozone  $A_N^R$ . The pseudo-first order decolorization rate constants, *k'*, decreased from aromatic ring number 2 ( $A_2^R$ ) to aromatic ring number 5 ( $A_5^R$ ).

## References

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