



CONFERENCE PAPER

Decolorization of Reactive Orange 16 and Reactive Black 5 in aqueous solution by ozonation

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ABSTRACT

Textile industry is one of the most chemically intensive industries on Earth and the major polluter of potable water. There are many methods for dye removal in the textile industry. One of the most effective methods is colour removal by ozonation. The application of ozonation has increased in recent years. Preference of the ozonation method is the efficiency of colour removal and the short application time. In ozonation process, not only colour but also the toxicity caused by products of treated wastewater is important. So, suitable ozonation period must be obtained. The aim of this study is the removal of Reactive Black 5 (RB-5) and Reactive Orange 16 (RO-16) from the synthetic aqueous solution by ozonation. In this study, dye removal (%) and chemical oxygen demand (COD) removal (%) were determined and carried out by kinetic analyzing. The maximum dye removals were 99.9 % and 99 % at all pH values in initial dye concentration of 100 mg L⁻¹ for RB-5 (40 min) and RO-16 (70 min), respectively. It was found that COD removal is 100 % for both dyes. Ozonation kinetics were studied and it was found that it agreed with the pseudo first order kinetics for two dyes. The highest pseudo first order kinetic constants are 0.1918 min⁻¹ (R²: 0.9978, pH:2) and 0.0794 min⁻¹ (R²: 0.9918, pH:6) for RB-5 and RO-16, respectively. The results obtained in this study showed that ozonation of reactive dyes at acidic or neutral pH was more suitable than that of alkaline pH.

Keywords: Ozonation, decolorization, chemical oxygen demand, Reactive Orange 16, Reactive Black 5

1. INTRODUCTION

The strong colour of textile effluent creates both environmental and aesthetic problems. It generates huge quantities of complex chemical substances as a part of unused materials including dyes in the form of wastewater during various stages of textile processing. The direct discharge of this wastewater into the water bodies like lakes, rivers etc. pollutes the water and affects the flora and fauna. Effluent from textile industries contains different types of dyes, which is because of high molecular weight and complex structures, shows very low biodegradability. The wastewater includes are both organic and inorganic structures after industrial processes. The dyestuffs used in the textile industry are generally azo dyes [1]. Azo dyes, which contain one or more azo bonds (-N=N-), are the most widely used synthetic dyes and generally are major pollutants in dyed wastewaters. Due to their toxicity and slow

degradation, these dyes are classified as environmentally hazardous materials. Azo dyes are normally hazardous to the environment even if they are present at low concentration [2].

Ozonation is an oxidative process in which ozone (O₃) is used as an oxidizing agent. Interest in the use of ozone in wastewater treatment has increased considerably in recent years. Ozonation has excellent potential in decolorization as decolorization and degradation occur in one step; danger to humans is minimal; no sludge remains; all residual ozone can be decomposed easily into oxygen and water; little space is required and ozonation is easily performed [3].

The treatment methods of textile wastewater are divided into three basic section; physical treatments, chemical treatments, and biological treatments. In the adsorption method which is one of the physical methods there must be affinity between the dye and the adsorbent. Even if this method is successful, solid

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waste problem occurs in the solution. Among the physical methods membrane separation technique is effective, but expensive, for example. Besides, frequent occlusions happen in the system. Biological methods usually contain biodegradation (aerobic or anaerobic), biosorption and bioaccumulation. The biomass used for biodegradation must consume the dye as carbon source. Biosorption requires biomass-dye affinity as the adsorption. As a result, solid waste is formed again. This situation is also similar in bioaccumulation. The chemical treatment methods include electrolysis, coagulation and electrocoagulation methods. Electrolysis is an expensive method. The coagulation method causes solid waste formation. The electrocoagulation method is similar according to this point of view. The most effective method applied today in chemical methods is the advanced oxidation process (AOP). AOP is based on the generation of powerful oxidants such as hydroxyl radicals [4]. Photocatalytic, photo-fenton, fenton, photocatalytic fenton and ozonation are the AOP. Ozone can degrade the complex structure of dye in a short time. Because of this reason, ozonation is rather an attractive technique on dye removal in recent years.

The ozonation process has been postulated as a potential, alternative method for decolorization and improvement of biological treatment. In literature, Zakaria et al. [5] studied decolorization of RO-16 by electrochemical oxidation and adsorption methods. They compared the effectiveness of these treatments and evaluated the percentage of RO-16 decolorization and COD removal. Their results indicated that electrochemical is the most effective method. RO-16 was decolorized up to 98.5 % after by this method. Tizaoui and Grima [6] investigated ozonation of RO-16 at different conditions (25-100 mg L⁻¹ dye; 20-80 g m⁻³, NTP ozone gas, pH: 2, 7, 11). They achieved up to 90 % decolorization yield for the initial concentration of 90 mg L⁻¹ between 20-80 g m⁻³ ozone gas concentration and 5-17 min ozonation time at pH 7. Also, they reported that degradation of the products are nitrosobenzene, nitrobenzene, benzene-1,4-diol, 1,4-benzoquinone, acetamide, phthalic, maleic, oxalic, acetic, formic acids. Şahinkaya [7] carried out the decolorization of RO-16 by ferrate (VI) oxidation assisted by sonication. It was found that dye removal efficiencies were 85 % by ferrate (VI) method and 91 % by sonoferrate (VI) method.

Venkatেশ et al. [8] studied the effect of ozonation on decolorization and mineralization of azo dyes (Acid Red 14, Congo Red, Reactive Black 5) at 1500 mg L⁻¹ initial dye concentration, 55.5 mg L⁻¹ ozone concentration and pH 10. The results showed that the COD and dye removal are 50 % and 94 % at 25 min ozonation time for RB-5, respectively. Wang et al. [9] examined the effect of ozonation on the degradation process of the RB-5. They studied at different experimental conditions (20.5 mg L⁻¹ ozone concentration, 2 g L⁻¹ initial dye concentration and pH 6). They found that the COD, total organic carbon (TOC) reductions were about 40 % and 25 % for 6 h ozonation. Venkatesh et al. [10] investigated for RB-5 ozonation followed by anaerobic biodegradation using up flow anaerobic sludge blanket (UASB)

reactor was carried out. Colour of dye solution declined exponentially with increase ozonation time at 1500 mg L⁻¹ initial dye concentration, 5 g h⁻¹ ozone flow rate, pH 10.13. It achieved around 70 % decolorization and 50 % COD reduction in 10 min. Decolorization efficiency was 94 % after 25 min of ozonation investigated in this study. The system of ozonation and anaerobic treatment by UASB reactor showed that the COD reduction has reached to about 90 % and dye removal 94 %, respectively.

Ozonation has been generally preferred for degradation of azo dyes due to the fact that ozone is highly reactive with azo double bond. Only one study [6] related to degradation of RO-16 by ozonation was found. A study of ozonation kinetic of RB-5 was not encountered in the literature. Also, it was observed that the COD removal for degradation of RB-5 was insufficient in the literature [8]-[10].

In the present study, in order to achieve high COD removal and colour removal for the effective degradation of RO-16 and RB-5, the effects of the ozonation time (0-150 min), the initial dye concentration (100-300 mg L⁻¹) and the initial pH (2-10) on the dye concentration and dye removal were investigated. The reason for the preference of Reactive Black 5 and Reactive Orange 16 (two types of azo dyes) is that they have complex chemical structures with various azo aromatic groups. Reactive Black 5 is a diazo dye and Reactive Orange 16 is a monoazo dye. The changing of pH of dye solutions with time were observed in the different initial dye concentrations. Also, the chemical oxygen demand (COD) removals were measured for 100, 200 and 300 mg L⁻¹ initial dye concentrations and 2, 6, 10 initial pH of solutions at the end of ozonation. Furthermore, the kinetics of ozonation for two dyes were investigated at the different initial dye concentrations and pH values.

2. MATERIALS AND METHODS

2.1. Dyes

Reactive Black 5 and Reactive Orange 16 were purchased from Sigma Aldrich Company. In the preparation of the dye solutions, distilled water was used. Table 1 shows the chemical structure and properties of Reactive Black 5 and Reactive Orange 16 used in this study [11].

2.2. Experimental Procedure

The ozone was generated from dry air in a laboratory model ozone generator (BNP Ozone, Model: 5) with a maximum capacity of 5 g h⁻¹. Fig 1 shows the schematic diagram of ozonation apparatus. Ozonation experiments were carried out in 500 mL glass reactor with 250 mL volume of dye solution. All the experiments were performed at room temperature (25 ± 2 °C), and in semi batch mode by sparging ozone continuously into the solution. Magnetic stirrer was used in the ozonation experiments. The chosen initial dye concentrations in the experiments were 100 mg L⁻¹, 200 mg L⁻¹ and 300 mg L⁻¹. Ozonation

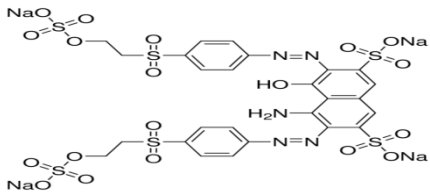
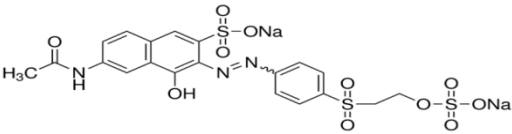
experiments at different pH values were conducted in order to observe the effects of acidic and basic pH values on the ozonation reactions and pH were adjusted with 1 M H₂SO₄ and 1 M NaOH. The samples were withdrawn from the reactor in every 10 minutes and the concentrations of dyes in their solutions were determined by spectrophotometric method (Shimadzu UV-1601 Spectrophotometer). The percentages of dye and COD removal was determined by using the following equation:

$$\text{Dye removal (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

$$\text{COD removal (\%)} = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \times 100 \quad (2)$$

In equation (1), C₀ and C_t are the dye concentrations (mg L⁻¹) at the beginning and t time (every 10 minute) of ozonation, respectively. In equation (2), (COD)₀ and (COD)_t are the chemical oxygen demand values at the beginning and end of ozonation, respectively.

Table 1. Structure and properties of Reactive Black 5 and Reactive Orange 16 [11]

Product Name	Structure	Formula	Molecular weight (g mol ⁻¹)	λ _{max} (nm)
Reactive Black 5		C ₂₆ H ₂₁ N ₅ Na ₄ O ₁₅ S ₆	991.82	597
Reactive Orange 16		C ₂₀ H ₁₇ N ₃ Na ₂ O ₁₁ S ₃	617.54	494

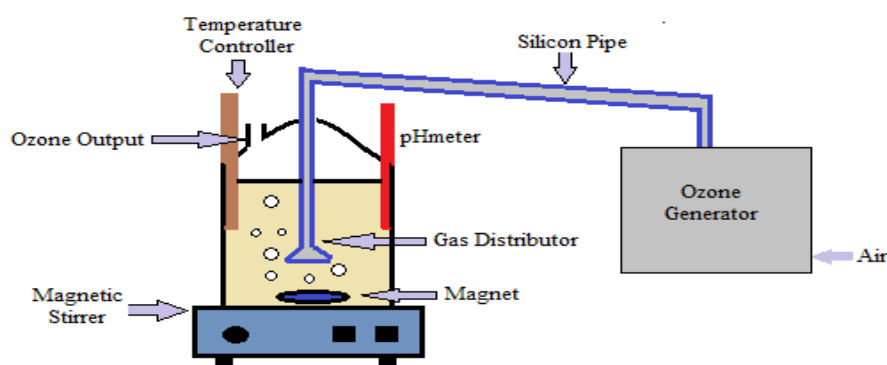


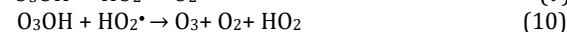
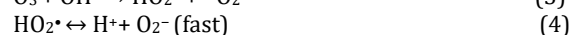
Fig1. Diagram of ozonation system

2.3. Analytical Methods

The samples were diluted with distilled water when required and the absorbance value was measured on the UV device. UV-VIS spectra of dye solution were recorded between 400 and 800 nm using double beam equipped with 2 mL plastic cuvette. The wavelengths of maximum absorbance (λ_{max}) were 597, 494 nm for RB-5 and RO-16, respectively. Chemical oxygen demands (COD) of the samples were measured by adding 2 mL of the sample solution into a glass vial containing 3 mL of COD standard solution and digesting the sample in a Lovibond Thermoreactor RD 125 for 2 h at 150 °C according to the standard methods (APHA 5220 COD) [12]. After the sample was cooled, its COD value was determined directly by a Lovibond Water Testing Tintometer Group MD 200. pH was measured by pH analyzer (Isolab Model 616.01.001 microprocessor-based waterproof pH/mV/Temp).

3. RESULTS & DISCUSSION

The decomposition reactions of ozone in pure water were reported in the literature [10], [13]-[18]. The reactions of decomposition mechanism of ozone in aqueous solution has been described by Hoigne, Staehelin and Bader (HSB model). Related reactions were given in following:



The reactions of organic molecule, M (M is dye in this study), with ozone in aqueous solution were given as explained with HSB model in literature:



As it is shown in above equations, the radicals as HO_2^\bullet , HO_3^\bullet , OH^\bullet and radicals ions $\bullet\text{O}_2^-$, $\bullet\text{O}_3^-$ or active specie as O_3OH were produced in this medium. Thus, it is too hard to explain the decomposition of organic molecule by ozone in textile wastewater. The effects of different parameters on dye removal and COD removal were investigated in order to facilitate the understandability of dye decomposition.

3.1. The Effect of Initial Dye Concentration on Dye Removal

The effect of initial dye concentrations and initial pH values on dye removal for RB-5 and RO-16 were investigated. Change of dye removal with ozonation time for two dyes were given in Fig 2 and Fig 3 (a,b,c). It was observed that dye removal increased with time in all cases of dye samples. For RB-5; it was observed that the ozonation time of 40 min is sufficient for maximum dye removal (99.9 %) at all pH values in low initial dye concentration (C_0 : 100 mg L⁻¹). However, ozonation time increased more 20 min (total 60 min) at high initial dye concentrations (200-300 mg L⁻¹) at all pH values (Fig 2-a,b,c).

For RO-16; maximum dye removal (99 %) was observed at 70 min in low initial dye concentration (C_0 : 100 mg L⁻¹ and at all pH values. Also, in initial dye concentrations of 200 and 300 mg L⁻¹ maximum dye removal (99 %) was observed at the end of 90 min for pH values of 2 and 10. This removal was obtained at the end of 150 min for pH value of 6 (Fig 3-a,b,c). According to Shu and Huang [19] and Muthukumar et al., [20] the time taken for complete decolorization of dyes by ozone increases with number of azo groups, while it decreases with increase number of sulfonic acid groups in the dye structure.

3.2. Changing pH of the Reaction Medium with Ozonation Time

In this section, changing pH of medium during ozonation was investigated. Related experimental results were given in Fig 4-a,b. As it is shown in this figure, while initial value pH of dye solutions was about 6 at all initial dye concentrations for RB-5 and RO-16, they reached acidic pH values (about 2) at the end of ozonation. We thought that it happened due to formation of molecules which have acidic structure at the end of ozonation.

Data in literature guides this hypothesis. The products of decomposition of RB-5 was reported as 5-aminonaphthalene-1,4 diol, 2,2'-Biphenyl-4,4'-diylldiacetic acid, N-formylformamide, (4-Nitrosophenyl) acetaldehyde, Muconic acid, (2Z)-pent-2-enedioic acid, Maleic acid by He et al. [4] Also, the products of decomposition of RO-16 was reported as nitrosobenzene, nitrobenzene, benzene-1,4-diol, 1,4-benzoquinone, acetamide, phthalic, maleic, oxalic,

acetic, formic acids. As it is shown that by-products have generally acidic structure. High colour removal is achieved at low pH. In acidic solution, the dye ozonation is performed by the direct mechanism. The degree of decolorization is favored by direct ozone attack, at low pH, since molecular ozone selectively attacks chromophore groups [17]. Also, in the study, it was observed that pH of dye solutions decreased (from 6 to 2) and dye removal increased (99.9 %) during ozonation (Fig 2 and 3). Moreover, similar results were obtained by Venkatesh et al. [8], [10].

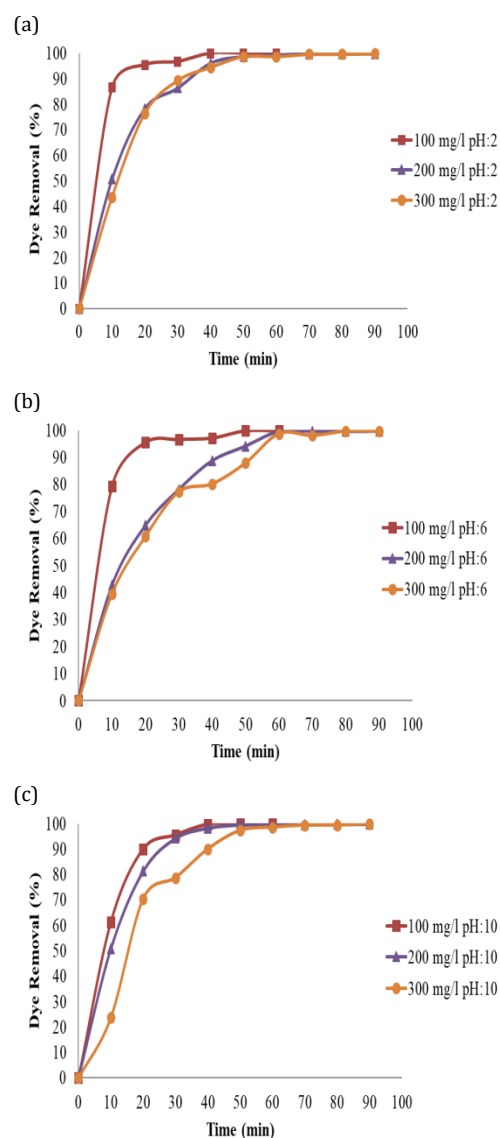


Fig 2. The changing of dye (RB-5) removal with ozonation time at different initial dye concentrations and pH ($Q_{O_3}=5\text{g h}^{-1}$, $T=25\pm 2^\circ\text{C}$) (a) pH:2; (b) pH:6; (c) pH:10

3.3. The Effect of Initial Dye Concentrations on COD Removal

COD values were measured at different initial dye concentrations and their ozonation time at pH values of 2, 6, 10 for RB-5 and RO-16 and COD removal values (%) were calculated. All the data of COD and COD removal were given at Table 2 and Fig 5-a,b.

In the study, COD removals are independently satisfactory (35-100 %) initial dye concentrations at neutral and acidic pH values for two dyes. On the other hand, it was observed that COD removals are low (30-70 %) at high pH values for dyes examined. Both RB-5 and RO-16 provided the highest COD removal (99, 100 %) at initial dye concentration of 200 mg L⁻¹ at neutral pH values. If changing COD removal with ozonation time is investigated, it is seen

that there is an increase first and decrease later. It was thought that it happened due to small organic molecules which are not completely degradable under the oxidative conditions. It could be said that high ozone flow rate (5 g h⁻¹) may cause the reduction of COD. Similar results were encountered in literature [8], [10].

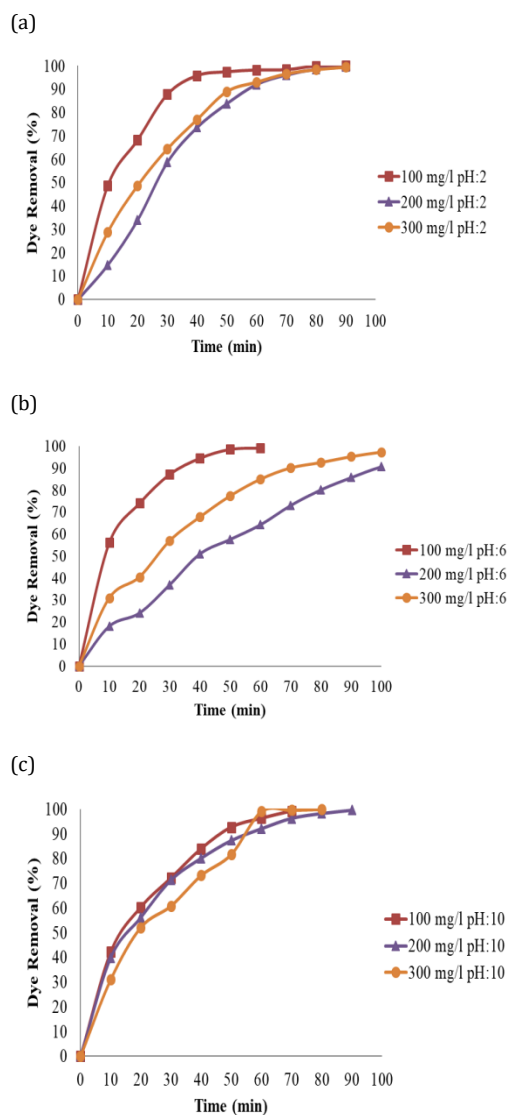


Fig 3. The changing of dye (RO-16) removal with ozonation time at different initial dye concentrations and pH ($Q_{O_3}=5g\ h^{-1}$, $T=25\pm 2\ ^\circ C$) (a) pH:2 ; (b) pH:6 ; (c) pH:10

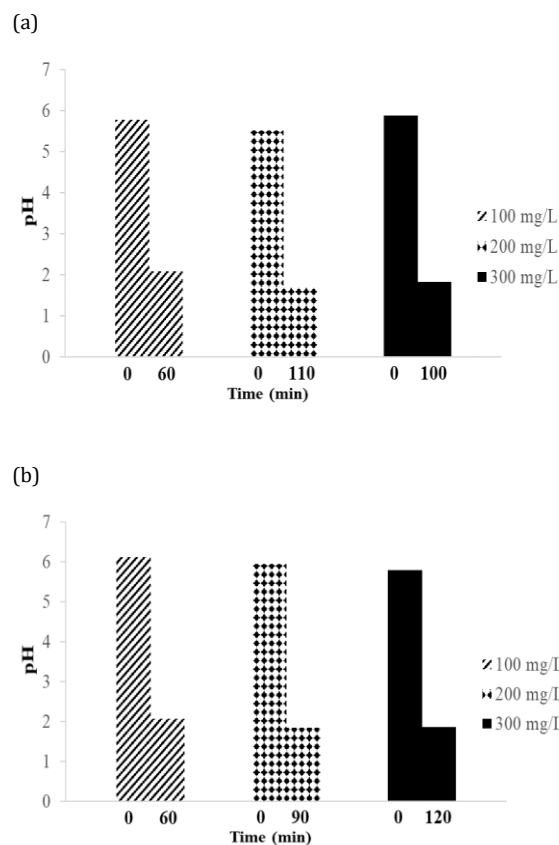


Fig 4. Changing pH at 25 °C with ozonation time for initial dye concentration:100, 200, 300 mg L⁻¹ (a) RB-5 and (b) RO-16

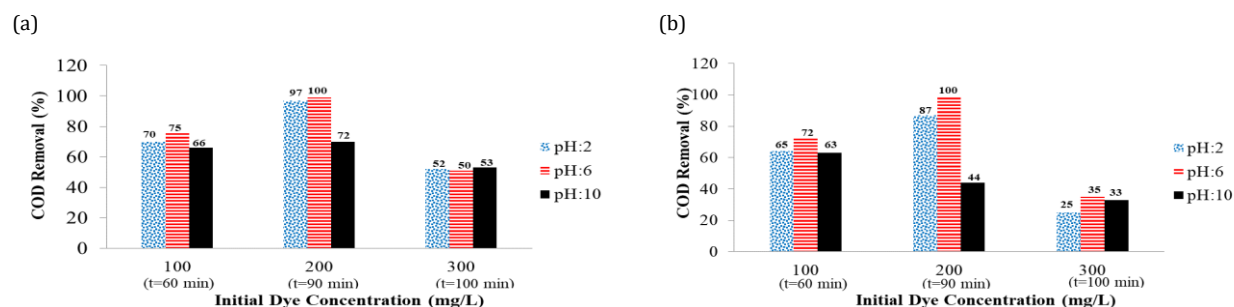


Fig 5. The efficiency of COD removal end of the ozonation for different initial dye concentration (100, 200, 300 mg L⁻¹) and initial pH values (2, 6, 10) (a)RB-5 (b)RO-16

Table 2. The influent and effluent concentrations of COD and COD removals for RB-5 and RO-16 at the different initial dye concentrations and pH values

RB-5					RO-16				
Initial Dye Concentrations (mg L ⁻¹)	pH	COD (influent)	COD (effluent)	COD % Removal	Initial Dye Concentrations (mg L ⁻¹)	pH	COD (influent)	COD (effluent)	COD % Removal
100	2	94	28	70	100	2	74	26	65
	6	53	13	75		6	60	17	72
	10	105	36	66		10	64	24	63
200	2	81	2	97	200	2	258	32	87
	6	167	0	100		6	207	0	100
	10	130	36	72		10	170	95	44
300	2	161	77	52	300	2	204	153	25
	6	129	64	50		6	200	130	35
	10	130	61	53		10	219	146	33

Table 3. Pseudo-first-order kinetic constants of RB-5 and RO-16 at different pH and different initial dye concentration

Dye Concentration (mg L ⁻¹)		pH: 2		pH: 6		pH: 10	
		RB-5	RO-16	RB-5	RO-16	RB-5	RO-16
100	R ²	0.9978	0.9827	0.9765	0.9818	0.9801	0.9783
	k	0.1918	0.0710	0.1314	0.0794	0.1481	0.0510
200	R ²	0.9854	0.9368	0.9703	0.9522	0.9691	0.9778
	k	0.0847	0.0366	0.0618	0.0215	0.0838	0.0457
300	R ²	0.9836	0.9679	0.9490	0.9846	0.9490	0.9328
	k	0.0739	0.0440	0.0519	0.0332	0.0519	0.0414

3.4. Ozonation Kinetics of RB-5 and RO-16

The process of ozonation happens because of oxidation by ozone molecules and by generation of hydroxyl radicals, which react with initial compound and intermediates. When the amount of ozone is excess or when the ozone concentration is assumed to reach a stationary state at the interface, the oxidation rate follows a pseudo-first-order kinetics with respect to the concentration of the organic substance in terms of degradation and the rate equation is as follows [21]:



where the rate constant k' can be determined by

$$-\frac{d[C_A]}{dt} = k'[C_A][O_3] \quad (18)$$

Eq. (18) can be simplified and k takes the form of an apparent pseudo first-order constant k if we assume that the concentration of very reactive O_3 radicals takes on a steady-state value during the process:

$$-\frac{d[C_A]}{dt} = k[C_A] \quad (19)$$

where k is pseudo-first-order rate constant and C_A is concentration of organic substance. On integration, the above equation is as follows:

$$\ln(C_A/C_{A0}) = -kt \quad (20)$$

The plot of $\ln(C_A/C_{A0})$ with reaction time (t), for decolorization of RB-5 and RO-16 during ozonation in Fig 6 was given. The reaction kinetics of ozonation at pH 2, 6 and 10 were investigated for RB-5 and RO-16, respectively. $\ln(C_A/C_{A0})$ versus time (t) curves (Fig 6-a,b,c) were found to be linear indicating a pseudo-first-order reaction at the equilibrium concentration of ozone in the aqueous phase for each pH (for pH range studied) and for both of the dyes. Oxidizing ability of ozone comes from either molecular ozone or hydroxyl free radical. The correlation coefficients (R^2) obtained were between 0.93 and 0.99.

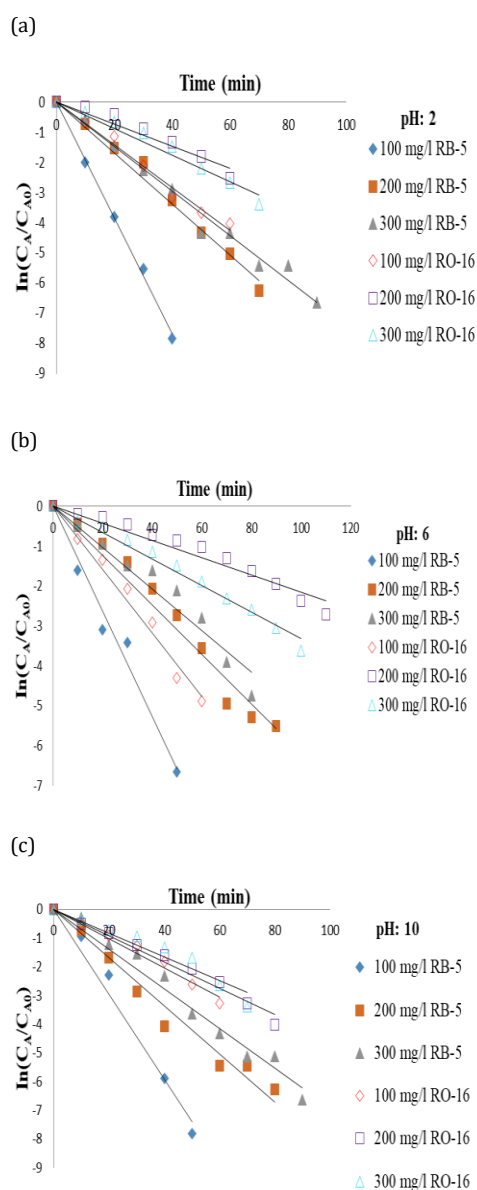


Fig 6. Linear transforms: $\ln(C_A/C_{A0})$ versus time for decolorization of RB-5 and RO-16 during ozonation (a)pH:2 (b)pH:6 (c)pH:10 ($Q_{O_3}=5 \text{ g h}^{-1}$, $T=25\pm 2 \text{ }^\circ\text{C}$)

Pseudo-first-order kinetic constants obtained by Fig 6 were given in Table 3 for RB-5 and RO-16 at different pH and different initial dye concentrations. It was found that the highest kinetics constants and correlation coefficients are in initial dye concentration of 100 mg L^{-1} at all pH values for RB-5 and RO-16. Ozonation rate of RO-16 was slower than that of RB-5. As it is shown in Fig 2 and Fig 3, ozonation time of RO-16 was longer than that of RB-5. The highest pseudo-first-order kinetic constants are 0.1918 min^{-1} ($R^2: 0.9978$, pH:2) and 0.0794 min^{-1} ($R^2: 0.9818$, pH:6) for RB-5 and RO-16, respectively.

He et al. [4] investigated decolorization of RB-5 by combined sonolysis and ozonation. They found that ozonation kinetic agreed with pseudo-first-order kinetic. Rate constants obtained by them are 1.21 min^{-1} , 0.744 min^{-1} and 0.636 min^{-1} at pH value of 11 and $35 \text{ }^\circ\text{C}$ for initial dye concentration of 100, 200, 300 mg L^{-1} , respectively.

The studies investigating ozone kinetics of RO-16 in wastewaters are insufficient in literature. The only one is the study of Tizaoui and Grima [6]. They carried out ozone oxidation RO-16 in aqueous solution. They reported that the reaction was assumed in the second order and Danckwerts model was used to determine the values of its rate constants.

4. CONCLUSIONS

The high volume of coloured wastewater in textile finishing industry demands a special treatment and evaluation of the ecotoxic effects of the process effluents released into the environment. Ozone treatment proves to be very effective for complete removal of colour, but provides only partial reduction of COD. Generally, ozonation is a potential technique for decolorization and COD removal of wastewater containing reactive dyes. In ozonation processes, not only colour but also the toxicity caused by products of treated wastewater is important. So, suitable ozonation period must be obtained.

In this study ozonations of Reactive Black 5 and Reactive Orange 16 were studied at initial dye concentrations of $100\text{-}300 \text{ mg L}^{-1}$, pH values of 2, 6, 10, ozone flow rate 5 g h^{-1} , temperature $25\pm 2 \text{ }^\circ\text{C}$. It was observed that dye concentration decreased and dye removal (%) increased with ozonation time at all experimental conditions. The maximum dye removals were 99.9 % and 99 % at all pH values in initial dye concentration of 100 mg L^{-1} for RB-5 (40 min) and RO-16 (70 min), respectively. It was found that COD removal is about 100 % for both dyes. The length of ozonation time and the high flow rate ozone caused the mineralization. Ozonation kinetics were studied and it was found that it agreed with the pseudo-first-order kinetics for two dyes. Removal of RB-5 by ozonation is faster than that of RO-16 according to obtained rate constants. The results obtained in this study showed that ozonation of reactive dyes at acidic or neutral pH was more suitable than that of alkaline pH. The results illustrated that high colour and COD removal were achieved at initial dye concentration of 200 mg L^{-1} and acidic/neutral pH and quite short ozonation time. Reactive dye required low energy for

decolorization and mineralization compared to other dyes. The conclusions of the present study have clearly revealed that ozonation has been proved to be a viable technique for the treatment of highly recalcitrant azo dyes containing wastewater.

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