Global NEST Journal, Vol 23, No X, pp 143-151

Determination of optimal conditions in decolorization of disperse dyes in aqueous solution by ozonation

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Received: 06/03/2019, Accepted: 11/04/2021, Available online: 20/05/2021
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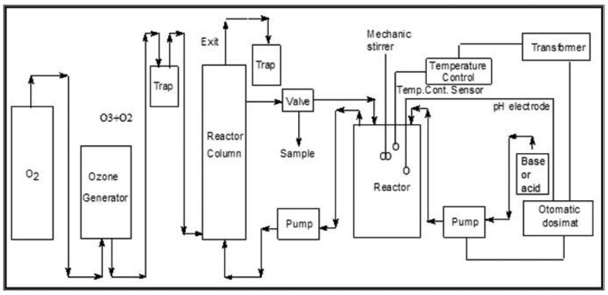
https://doi.org/10.30955/gnj.003096

Graphical abstract



Abstract

In this study, water-soluble disperse dyes [Disperse Violet 93 (DV93); Diffused Blue 79 (DB79); Disperse Orange 30 (DO30)] color removal by ozonation, which is one of the advanced treatment methods of synthetic dye waste solutions containing and whose decolorization conditions have not been investigated before, were investigated and the most suitable parameter criteria were determined. The experiments were carried out using a semi-batch reaction. The decolorization process of the reactive dye was carried out by bubbling ozone at the bottom of a bubble column reactor containing the dye solution. The effects of the ozonation time (0-120 min), the initial dye concentration (150-600 mg/L), ozone concentration (4.21-24.03 g/m^3), the initial pH (2-12), and decolorization time was studied. As a result, COD values obtained from color measurements determined by the spectrophotometric method of disperse dye wastewater prepared synthetically after optimum conditions were achieved in experiments decreased by 61.05%, 72.88%, and 77.43%, respectively, and a significant color removal occurred under basic conditions (pH: 10 for DV93 and DB79; pH: 12 for DO30). For each dye processed separately, decolorization occurred within 16 minutes, 12 minutes, and 9 minutes, respectively. Ozonation kinetics were studied and it was found that decoloring showed first-order kinetics for the three dyes. The study showed that the apparent rate constant increased both at the applied ozone dose and under basic conditions, and decreased logarithmically with respect to the initial dye concentration. As a result of the study, it was determined that ozonation is a usable method for the treatment of azo dyes in textile wastewater; optimum conditions were determined for parameters such as the shortest time, optimum ozone dose, and appropriate pH range.

Keywords: Ozonation, disperse dye, chemical oxygen demand, kinetics, decolorization.

1. Introduction

Synthetic dyes are commonly used in many commercial areas such as cosmetics, leather tanning, food processing, textile, plastic, paper, printing, and dye manufacturing industries (Lofrano *et al.*, 2013; Yagub *et al.*, 2014). These dyes can be regarded as pollutants arising due to their potential toxicity and presence in the aquatic environment; and unfortunately, there are no regulations that specify the maximum permissible concentrations in water to ensure the protection of aquatic biota and human health (Ribeiro and Umbuzeiro, 2014). Reactive and disperse dyes in the textile market meet almost half of the world's dye demand. During the dyeing of the textile material, some of the dye is not bound to the fibers and remains in the water bath. For this reason, large volumes of wastewater containing dyes and related auxiliaries are generated and can be released into the environment. Since the wastewater discharged into the environment cannot be removed by nature, there is significant pollution in the water. This reduces the permeability of sunlight, prevents the photosynthesis of aquatic plants, and seriously threatens the ecological system (Ghaly *et al.*, 2014; Golka *et al.*, 2004; Ribeiro and Umbuzeiro, 2014; Umbuzeiro *et al.*, 2005).

Disperse dyes belonging to the class of azo compounds derived from certain aromatic amines are the most commonly used dyes for coloring polyester, nylon, acetate, cellulose, and acrylic fibers (Bardi and Marzona, 2010). This class of diazo and triazo structured disperse dyes are very popular due to their easy application, wide color range, and low cost. Because of their toxicity and power degradation, these dyes are hazardous to the environment, even if they are normally present at low concentrations. For this reason, it is necessary to find a suitable and efficient method to remove the color of the wastewater. The treatment methods of textile waste-water are divided into three basic sections; (i) physical (adsorption, coagulation-flocculation), (ii) biological (living or dead microbial cultures), and (iii) chemical (oxidative processes) (Van der Zee and Villaverde, 2005). In the adsorption method, which is among the physical methods, there must be an affinity between the dye and the adsorbent. Even if this method is successful, the solid waste problem occurs in the solution. Coagulation has been applied for many years in the treatment or pre-treatment of wastewater containing dyes due to its low cost (Gadekar and Ahammed, 2016; Verma *et al.*, 2012). However, it causes sludge production and cannot be effective in removing some soluble dyes (Hai *et al.*, 2007). If the small volume of highly colored wastewater formed after the dyeing process, the amount of sludge formed during the color removing process by coagulation is less. Water-soluble dyes are difficult to remove by coagulation. In addition, with the development of synthesis technol-ogies, many dyes with complex structures are synthesized and this situation creates a problem in choosing the correct coagulant (Verma *et al.*, 2012).

Membrane technology used in wastewater treatment plants offers advantages such as good quality of effluent, less space occupation, easy operation, less chemical needs compared to conventional systems, modular design, no effect on the form of the pollutant, chemistry, and low cost. However, the problem of clogging, which is one of the most important problems in the facilities using membranes, and the cost of equipment are important dis-advantages (Naghdali *et al.*, 2019; Naghdali *et al.*, 2020).

In recent years, the applications of electrochemistry to reduce environmental pollution have been extensively researched, especially the feasibility of electrochemical conversion/destruction of organic substrates in wastewater. In these studies, the effect of the nature of the electrode material during the anodic mineralization of organics was discussed in detail and it was shown that optimum conditions were obtained in high oxygen compared to potential anodes for the said process. However, this method; is not preferred because of its high cost, the electrolyte used may cause corrosion of the equipment, the necessity of a large production floor, and its environmental friendliness (Crini and Lichtfouse, 2019; Najafpoor *et al.*, 2017; Emamjomeh *et al.*, 2020; Palanisamy *et al.*, 2020).

Biological methods usually contain biodegradation (aerobic or anaerobic), biosorption, and bioaccumulation. The biomass used for biodegradation must consume the dye as a 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. Various bacterial consortia have been developed, including species capable of efficiently degrading azo dyes under bottle-scale conditions (Franciscon *et al.*, 2015). However, due to the low biodegradability of most dyes and chemicals used in the textile industry, effective removal cannot always be achieved with biological treatment (Bhatia *et al.*, 2017; Jaafari et al, 2019; Türgay *et al.*, 2011).

The most effective method applied today in chemical methods is the advanced oxidation process (AOP) with various oxidants such as O_3, O_3/UV, O_3/H_2O_2, O_3/US (Evelin *et al.*, 2019; Turhan *et al.*, 2012; Xingaoyuan *et al.*, 2019), UV/chlorine (Ghanbari *et al.*, 2020), Fenton's reagent (Askarniya et al, 2020), H_2O_2 (Salem *et al.*, 2014), UV (López-López *et al.*, 2007) and UV/H_2O_2 (Kaiheng *et al.*, 2018). In addition, a recent study used sodium formaldehyde sulfoxylate (SFS) to reduce the color of disperse dyes developed for polyethylene terephthalate (PET) (Fei *et al.*, 2020).

Ozone can degrade the complex structure of dye in a short time. Because of this reason, ozonation is one of the most effective alternatives to solve color problems in textile wastes (Soares *et al.*, 2007). In fact, the color of the dyestuff depends on the chromophore groups. Ozone is an excellent agent for the decomposition of chromophore groups in particular and is very effective for color removal of the dyestuff in wastewater (Choi *et al.*, 2004; Paprowicz and Slodczyk, 1998). Ozonization provides the perfect potential for both color removal and decomposition in one-step; the danger to living beings is minimal; does not form mud; all residual ozone, oxygen, and water can be easily separated; does not require large areas and is easy to apply ozonation (Brillas *et al.*, 2014).

In the present study, in order to achieve decolorization and high COD removal for the effective degradation of DV93, DB79 and DO30, the effects of the ozonation time (0-120 min), the initial dye concentration (150-600 mg/L), ozone concentration (4.21-24.03 g/m^3) and the initial pH (2-12) on the dye concentration and dye removal were investigated. The reason for the preference of DV93, DB79 and DO30 is that they have complex chemical structures with azo aromatic groups. The changing of pH of dye solutions with time was observed in the different initial dye concentrations. In addition, the chemical oxygen demand (COD) removals were measured for 150, 300, 450 and 600 mg/L of initial dye concentrations and 2, 4, 6, 8, 10 and 12 of initial pH of solutions at the end of ozonation. In addition, the kinetics of ozonation for three dyes were examined at different initial dye concentrations and at different pH values.

2. Materials and methods

2.1. Experimental part

The experimental scheme shown in Figure 1 contain an ozone generator, 5 cm (Ø) x 110 cm (h) cylindrical column reactor (2L), a reactor for dye solution (5L), a dosimeter, a temperature control unit, wash bottles, oxygen gas tube and peristaltic pumps. The laboratory-scale Fischer 502 model ozone generator was used for ozone production from oxygen. The temperature was kept at 20±1 ^{0}C in all experiments. Ozonation applications at different pH values were conducted in order to observe the effects of pH values on the ozonation reactions and pH were adjusted with 1 M H_2SO_4 and 1M 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 (Agilent 8453 Spectrophotometer). The percentages of dye and COD removal was determined by using the following equation (1) and (2) (Attar *et al.*, 2019):

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

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

In equation (1), C_0 and C_t are the dye concentrations (mg/L) at the beginning and at the t time of ozonation, respectively. In equation (2), $(\text{COD})_0$ and $(\text{COD})_t$ are the chemical oxygen demand values at the beginning and end of ozonation, respectively.

Unreacted ozone was sent from the top of the column reactor with a silicone hose to the washing bottles containing 2% KI solution (Turhan and Turgut, 2007; Turhan and Turgut, 2009a; Turhan and Turgut, 2009b; Turhan *et al.*, 2012; Turhan and Ozturkcan, 2013).

$$O_3 + 2KI + H_2O \rightarrow I_2 + 2KOH + O_2 \quad (3)$$

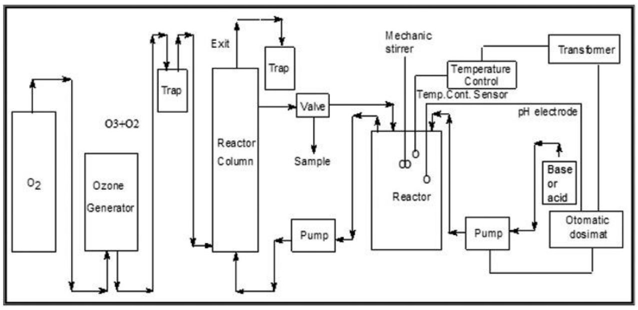
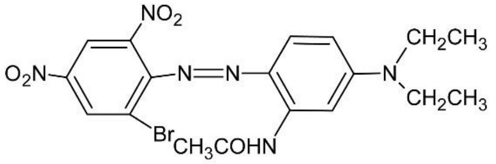


Figure 1. Schematic diagram of the bench-scale reactor system

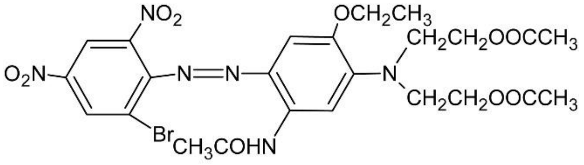
The amount of unused ozone was determined by titration of iodide with $Na_2S_2O_3$ in the presence of starch indicator as in our previous experience (Turhan and Turgut, 2007; Turhan and Turgut, 2009a; Turhan and Turgut, 2009b; Turhan *et al.*, 2012; Turhan and Ozturkcan, 2013). In addition, ozone flow rate and ozone concentration must be high in order to effectively treat wastewater by using ozone. Therefore, the experiments were performed at a 120 L/h ozone airflow rate.

2.2. Dyes

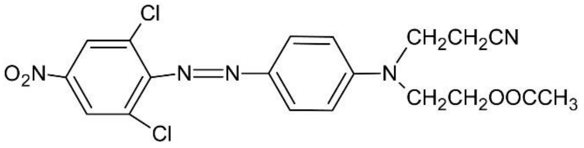
The dyes named commercially C.I. Disperse Violet 93, C.I. Disperse Blue 79 and C.I. Disperse Orange 30 were purchased from Setaş (Tekirdağ, Turkey). The characteristics of these dyes are shown in Table 1, and their general structures are shown in Figure 2. Dye solutions were prepared in water obtained from reverse osmosis at a concentration of 1000 mg/L. This stock solution was stirred for 30 minutes and then used to prepare dye solutions at the desired concentration.



Disperse Violet 93 (DV 93)



Disperse Blue 79 (DB 79)



Disperse Orange 30 (DO 30)

Figure 2. Structures of the disperse violet 93, disperse blue 79 and disperse orange 30

2.3. Equipments

UV/VIS spectra of dye solutions were recorded between 300 and 700 nm using double beam equipment with 1 mL quartz cuvette. The wavelengths of maximum absorbance (λ_{max}) were 560.7, 547.0 and 640.0 nm for DV93, DB79 and DO30, respectively. De-ionized water was used throughout the experiments for all solution preparations. The color of the dye solutions was measured by an improved integration method for COD measurement. This method involves scanning the absorbance of the sample between 300 and 700 nm and integrating the area under the absorbance curve. The integrated area is expressed as integral absorbance units (IAU) which are directly proportional to the sample color (Wu *et al.*, 1998; Wang *et al.*, 2003; American Public Health Association (APHA), 2005). Improved integration method used for COD measurement; Due to the large number of standard curves and complex equations used to calculate ADMI values, Kao *et al.* (2001) and Fazli *et al.* (2010) made measurements using Hach Lange DR5000 and Hach DR5000 spectrophotometers, respectively, for ADMI measurement. However, since the American Paint Manufacturers Institute showed that both methods yield similar results, the improved integration method was preferred.

Table 1. The characteristics of three azo dyes studied in this work

Disperse Dyes	Formula	CAS Number	λ_{max} (nm)	MW (g/mol)
C.I. Disperse Violet 93	$C_{18}H_{19}BrN_6O_5$	52697-38-8	560.7	479.29
C.I. Disperse Blue 79	$C_{24}H_{27}BrN_6O_{10}$	12239-34-8	547.0	639.41
C.I. Disperse Orange 30	$C_{19}H_{17}Cl_2N_5O_4$	12223-23-3	640.0	450.27

3. Results and discussion

3.1. Decolorization kinetics of DV93, DB79 and DO30

The reaction mechanisms of ozonolytic reactions follow two possible degradation paths. Both molecular ozone attack (i.e. direct reaction) and the free radical mechanism (i.e. indirect reaction) have been found to exist simultaneously during the reaction processes. At basic pH, ozone rapidly decomposes to yield the hydroxyl radical and other radical species in solution. Under acidic conditions, ozone can directly react with organic substrates as an electrophile (Wang *et al.*, 2003).

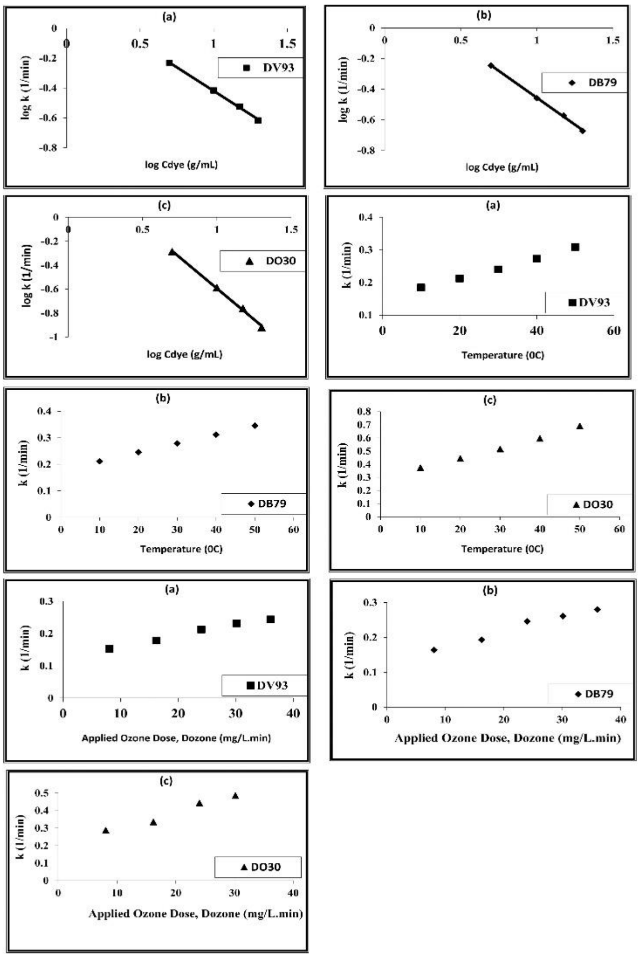


Figure 3. Dependence of the apparent rate constant of decolorization *k* on initial dye concentration, applied ozone dose and temperature for DV93, DB79 and DO30, respectively. **(a)** D_{ozone} = 24,03 mg/L.min, T = 20 ^{0}C **(b)** C_{dye} = 450 mg/L, T = 20 ^{0}C **(c)** C_{dye} = 450 mg/L, D_{ozone} = 24,03 mg/L.min

Pseudo-first-order trends typical for the ozone dye reaction were observed in all of the experimental runs. The rate constant k was defined by the graph slope using the kinetic equation for first-order reaction (ln C = -k.t + const) transformed into equation (4) (Saunders *et al.*, 1983; Carriere *et al.*, 1993; Wu and Wang, 2001):

$$k.\,t = \ln C_0 - C \qquad (4)$$

where, k: rate constant, 1/min, C_0: the initial dye concentration, mg/L, C: dye concentration at the specific time, mg/L.

Previously published data by Chu and Ma (2000), Demirev and Nenov (2005), and Turhan and Turgut (2007, 2009a) indicate that at the condition of constant ozone concentration, which is the case in our study, the ozonation becomes pseudo-first order with respect to the dye.

Equation (4) was used in the form of C = C_0. $e^{k.t}$, and it was calculated for the different C_0 based on the k graph values.

The line-fitted values of k for the pH and the corresponding dyes studied are given in Table 2.The above results clearly show that the rate of ozonation increases with the dye concentration. The effect of the initial dye concentration on the apparent rate constant was studied using the dependence log k = *f* (log C), as illustrated in Figure 3.

Similarly, the results obtained previously with wastewater containing a basic dye (Demirev and Nanev, 2005), the apparent rate constant (k_{app}) declined logarithmically with the initial dye concentration as in equation (5).

$$\begin{aligned} k_{app} &= 0.2123 \times C_{DV93}^{-0.6316} \\ k_{app} &= 0.2461 \times C_{DB79}^{-0.702} \\ k_{app} &= 0.4429 \times C_{DO30}^{-1.0371} \end{aligned} \qquad (5)$$

where, k_{app}: apparent rate constant, 1/min, C_{dye}: the initial dye concentration, mg/L (for DV93, DB79 and DO30).

As can be seen in Table 2, higher rate constants were obtained at this pH, so a basic pH environment was preferred for optimum parameters. The parameters of ozonation time, initial dye concentrations, ozone concentration and initial pH, which are the most remarkable and primarily important in terms of ozonation cost, were discussed. In addition, the wastewater temperature above 35°C increases the rate of ozone decomposition into oxygen (Keqinng *et al.*, 1994). For this reason, it is clear that ozonation will be more effective in color removal at T < 35°C wastewater temperature. However, the temperature factor is not examined in this study because it brings costs.

3.2. The effect of pH of initial solution on COD

At the beginning of the ozone treatment, a solution of 450 mg/L was prepared 7000 mL of solution for each dye was placed in the reactor. Each dye solution was studied separately. The experiment was initiated when the ozone gas began to pass. In the experiments of all three dyes, samples were taken from the sample port at regular intervals to determine the COD concentration of each dye. The initial pH of the synthetically prepared disperse dye solutions was 6.4, 5.3 and 5.5 for DV93, DB79 and DO30, respectively. The COD of synthetic disperse dyestuff wastewaters were reduced from 1312 mg/L to 916 mg/L for DV93, from 1228 mg/L to 758 mg/L for DB79 and from 731 mg/L to 391 mg/L DO30 after ozonation for 2 hrs. Considering the effect of pH on these results, ozonation tests were performed for each synthetic dye wastewater and COD values were measured at various pH values (pH 2-12). The results obtained are shown in Figure 4.

Table 2. Line-fitted values of rate constant k, (1/min)

Disperse dye	**pH**	***k* (1/min)**			
		C_0 = 5 mg/L	**C_0 = 10 mg/L**	**C_0 = 15 mg/L**	**C_0 = 20 mg/L**
Disperse Violet 93	6.0	0.189	0.168	0.150	0.137
	8.0	0.254	0.223	0.196	0.172
	10.0	0.379	0.296	0.256	0.218
	12.0	0.586	0.384	0.299	0.242
Disperse Blue 79	6.0	0.262	0.214	0.179	0.141
	8.0	0.426	0.279	0.205	0.177
	10.0	0.569	0.348	0.268	0.213
	12.0	0.511	0.317	0.248	0.204
Disperse Orange 30	6.0	0.297	0.218	0.153	0.098
	8.0	0.429	0.316	0.208	0.112
	10.0	0.515	0.258	0.173	0.120
	12.0	0.498	0.369	0.263	0.161

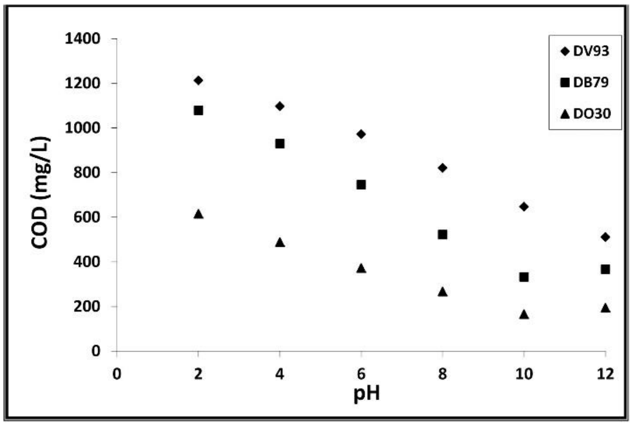


Figure 4. Effect of pH of the initial solution on COD (COD raw disperse dyestuff: 1312 mg/L for DV93, 1228 mg/L for DV79, 731 mg/L for DO30; Ozone conc.: 24 g/m^3; Dye concentration: 450 mg/L; Dye solution: 7000 mL; Ozone-air flow rate: 120 L/h; Ozonation time: 120 min.)

The decolorization time is inversely proportional to the pH of the starting solution. Figure 5 shows the effect of decolorization of the dye on the starting dye solution at different pH by using the COD values found. According to Elovitz and von Gunten (1999), the pH affects ozone degradation and the ozonation process by affecting the speed of ozonation kinetics. At basic pH, the degradation of ozone prefers to proceed through the formation of hydroxyl radicals. This explains that when the pH value changes from 2 to 12 for each of the DB79, DO30 and DV93 dye solutions, the dye dissolution time is highest under basic conditions and decreases by 56.55%, 61.49% and 67.05% respectively. Results obtained with dyestuff effluents showed that reduction of color removal (or COD) at pH 10-12 was the best conditions. After 120 minutes of ozonation reaction, it showed that the decrease of the COD of the dye effluent was noticeable at pH 10-12. Therefore, pH 12.0 for DV93, pH 10.0 for DB79 and pH 10.0 for DO30 was chosen as the optimum pH for subsequent experiments.

3.3. Spectrophotometric investigation of the process

The UV-Vis spectra after ozonation of DV93, DB79 and DO30 dye solutions are shown in Figure 6. Absorbance values of solutions of maximum wavelengths (λ_{max} = 560.7 nm (DV93), 547.0 nm (DB79) and 640.0 nm (DO30)) were measured at the specific wavelength of dyestuff solutions. The results showed that the color of the dyes were rapidly deteriorated and removed at the reaction times of 32, 28 and 16 minutes, respectively. Therefore, it was accepted that dye solutions DV93, DB79, and DO30 were successfully decolorized in 32, 28, and 16 minutes, respectively, by ozonation. However, although the color was removed at these times, the experiments were continued for 120 minutes, as the aromatic structure was spectroscopically observed for up to 120 minutes.

3.4. Effect of reaction time

The COD values of DV93, DB79 and DO30 against ozonation in different reaction times at varying pH ranges (pH 10-12) to the dye solution (ozone concentration: 24 g/m^3; dye concentration: 450 mg/L; dye solution: 7000 mL); ozone-Air flow rate: 120 L/h) measured. As can be seen in Figure 7, since there was no significant difference in the COD values of the dye solution after 120 minutes, this time was accepted as the best time for ozonation. After 120 minutes of ozonation reaction, the decrease in the COD values of the dye effluents was 61.05% (at pH 12.0) for DV93, 72.88% for DB79 (at pH 10.0) and 77.43% (at pH 10.0) for DO30.

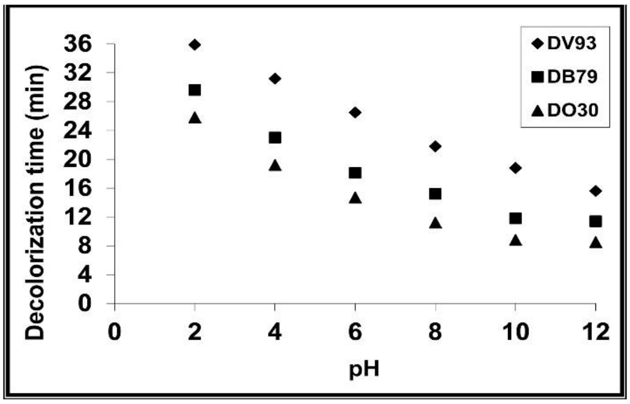


Figure 5. Effect of initial solution pH on decolorization time (Dye conc.: 450 mg/L; Dye solution: 7000 mL; Ozone-air flow rate: 120 L/h; Ozone conc.: 24 g/m^3)

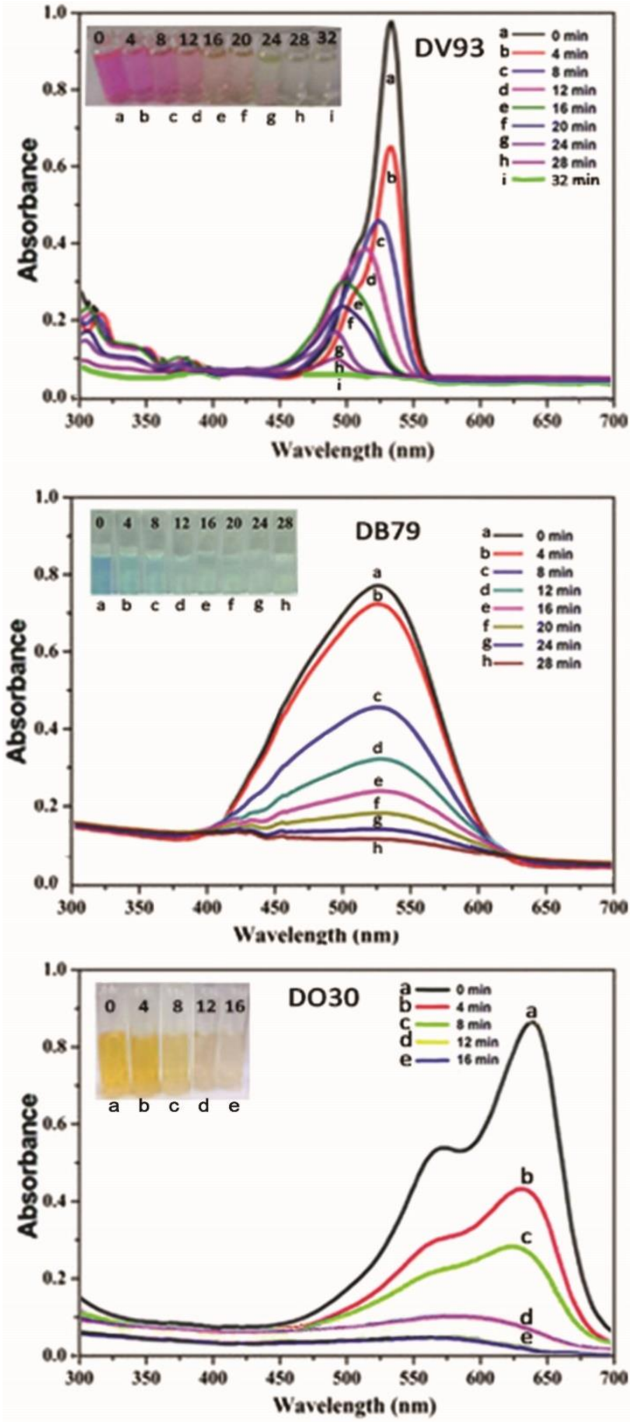


Figure 6. UV–Vis spectra changes of DV93, DB79 and DO30 (450 mg/L) with ozone after different reaction time at initial pH (pH 12.0 for DV93, DB79 for pH 10.0 and DO30 for pH 10.0)

3.5. *Change in dye concentration versus ozonation time at different initial concentrations of the dye*

Figure 8 plots the change in dye concentration versus ozonation time at four different initial concentrations of 150 mg/L, 300 mg/L, 450 mg/L and 600 mg/L for each dye. As can be seen from the graph, dye solutions DV93, DB79 and DO30 were considered to be successfully decolorized by ozonation in 32, 28 and 16 minutes, respectively.

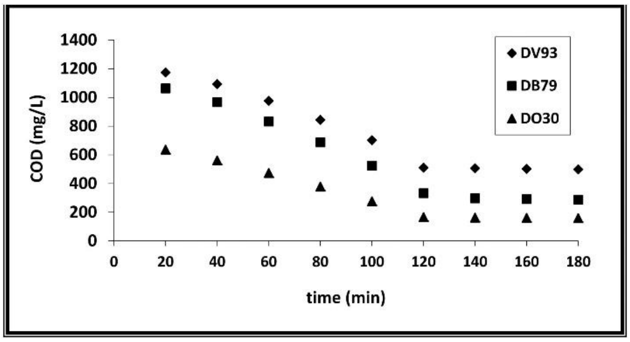


Figure 7. COD values of DV93, DB79 and DO30 with ozone after different reaction time at pH 10-12. (Ozone conc.: 24 g/m^3; Dye concentration: 450 mg/L; Dye solution: 7000 mL; Ozone-air flow rate: 120 L/h)

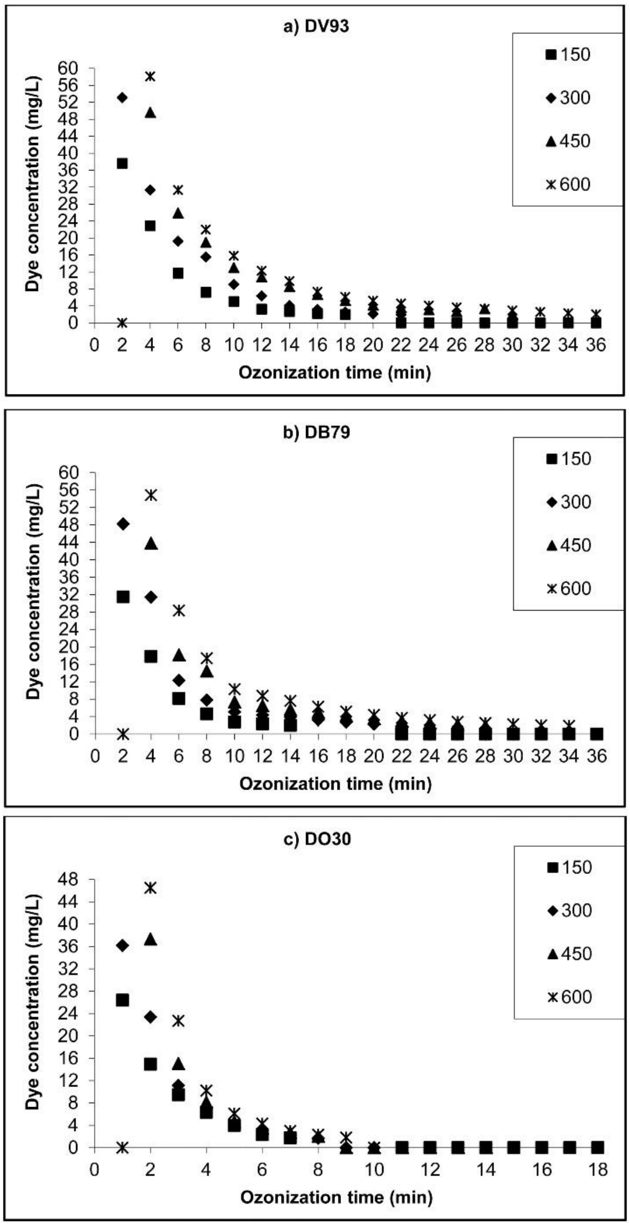


Figure 8. Graphs of change in dye concentration versus ozonation time at different initial concentrations of dyes (Ozone conc.: 24 g/m^3; Dye solution: 7000 mL; Ozone-air flow rate: 120 L/h) **a)** DV93 (pH: 12); **b)** DB79 (pH: 10); **c)** DO30 (pH: 10)

3.6. Effect of initial dye concentration on the decolorization time of DV93, DB79 and DO30 or each dye treated by ozone

The graph in Figure 9 shows the time required for decolorization versus initial dye concentrations for the three dye solutions. As shown in the graph, the decolorization time is in direct proportion to the initial dye concentration in the wastewater.

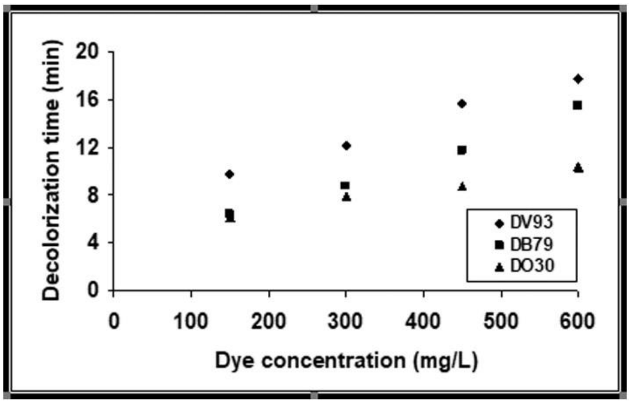


Figure 9. Effect of initial dye concentration on the decolorization time of DV93, DB79 and DO30 or each dye treated by ozone (Ozone conc.: 24 g/m^3; Dye solution: 7000 mL; Ozone-air flow rate: 120 L/h; pH: 12 for DV93; pH: 10 for DB79; pH: 10 for DO30)

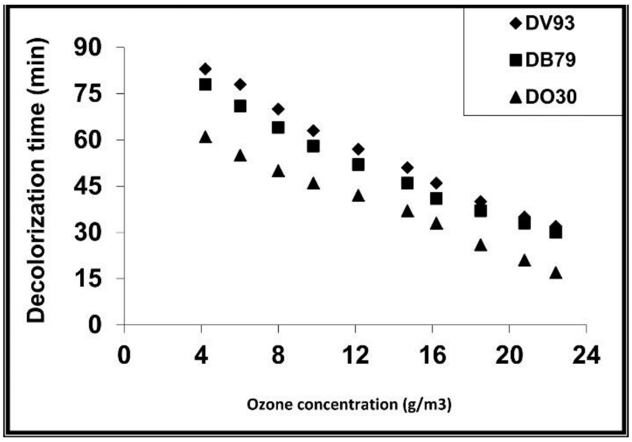


Figure 10. Effect of ozone concentration on dye decolorization time (Dye conc.: 450 mg/L; Dye solution: 7000 mL; Ozone-air flow rate: 120 L/h; pH: 12 for DV93; pH: 10 for DB79; pH: 10 for DO30))

3.7. Effect of ozone concentration on dye decolorization time

The ozone concentration and decolorization time graph is given in Figure 10. As can be seen in the graph, when the ozone concentration increases, the decolorization time decreases. For example, for 450 mg/L DO30 solution, the decolorization time was reduced by approximately 73.8% by increasing the ozone concentration from 4.21 g/m^3 to 24.03 g/m^3. This result is consistent with mass transfer theories (Raghuvanshi *et al.*, 2005). According to these theories, as the ozone concentration increases in the air bubbles, the driving force for transferring ozone to the dye solution increases with the increase in the ozone concentration in the solution and the dye oxidation rate. High ozone concentrations were effective for the reduction of COD.

4. Conclusion

High colored wastewater in the textile finishing industry requires the evaluation of the ecotoxic effects of process wastes released by a particular treatment to the environment. Ozone treatment has proven to be very effective for complete removal of color, but only to a partial reduction of COD. In general, ozonation is a potential technique for color removal and COD removal of wastewater containing disperse dyes. In ozone processes, toxicity caused not only by color but also by purified wastewater products is also important. Therefore, suitable ozonation conditions should be obtained.

In this study, the aqueous solutions of a model textile disperse dyes (DV93, DB79, and DO30) were ozonated in a semi-batch reactor. An experimental study was conducted to assess the efficacy of indirect type ozonation by radical type reactions to increase the labile degradability of aqueous solutions of a DV93, DB79 and DO30 model of stubborn contaminants. A detailed review of the results allows us to give the following results:

- ➢ For DV93, DB79 and DO30, the COD ratio of disperse dyestuff wastewater after ozonation decreased to 61.05%, 72.88% and 77.43%, respectively. Results obtained with disperse dyes showed that COD reduction and decolorization were remarkable at pH 10-12.
- ➢ The results obtained with disperse dyes found that the reduction in COD ratio and the best decolorization were at pH: 12 for DV93, at pH: 10 for DB79, at pH: 10 (under basic conditions) for DO30. High ozone concentration was effective in reducing COD values.
- ➢ Ozone consumption continued for 32 min, 28 min and 16 min, respectively. It was clear that high ozone concentration had a great effect on COD reduction. These results are consistent with the time (determined by checking with spectroscopic measurements) the aromatic structure contained in disperse dye solutions subjected to ozonization.
- ➢ Ozonation kinetics agreed with the pseudo-first-order kinetics for three dyes. Removal of DB79 by ozonation was faster than that of DV93 according to obtained rate constants, but slower than the DO30. The results obtained in this study showed that ozonation of disperse dyes at alkaline pH was more suitable than that of acidic or neutral pH. The results illustrated that high color and COD removal were achieved at the initial dye concentration of 450 mg/L and acidic/neutral pH and quite short ozonation time.

The proposed oxidation process has significantly reduced the Chemical Oxygen Demand (COD). The treated dye is less toxic and confirmed by phytotoxicity analysis. Importantly, this method can be scaled appropriately for industrial applications with appropriate adaptations to minimize toxicity found in industrial wastewater. As a result of this study, the ozonation process proved to be an applicable method for the treatment of azo dyes found in textile wastewaters. Further investigations are currently in progress to better elucidate the whole oxidation pathway as well as for evaluating the effect of ozonation on real samples of industrial wastewaters.

Acknowledgments

This work was supported by the Yıldız Technical University Scientific Research Projects Coordination under Grant Project Number 2013-01-02-GEP02.

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