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Decolorization of Reactive Yellow 17 in aqueous solution by ozonation

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Abstract: In this study, factors affecting removal of color by ozonation of synthetic dye solutions containing water-soluble reactive dye [Reactive Yellow 17 (RY17)] were investigated using chemical oxygen demand (COD) measurement method. The research was conducted using a semi-batch bubble column. As a result, the COD of the reactive dye wastewater was reduced by 78.58%, and decolorization was remarkable at pH 12, complete degradation of the dye solution occurs in 12 min, ozone consumption goes on for a further 30 min after which time most degradation reaction is completed. Kinetic study results have shown that direct ozonation of the dye solutions is a pseudo-first-order reaction with respect to dyes. The apparent rate constant increased both with applied ozone dosing and higher pH values, logarithmically decreased with the initial dye concentration.

Keywords: Ozonation, Reactive Yellow 17, Reactive Dye, Decolorization, COD.

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INTRODUCTION

One of the most important natural resources for living beings and vital water is threatening our world because of the water crisis that will come out with increasing human population, rapid industrialization, living standards, and consumption. One of these threatening factors is the textile industry, which consumes a high volume of wastewater. Textile wastewaters usually consist of many contaminant parameters such as acidic and basic solutions, water-soluble solids, toxic compounds, and coloring materials. Even at low concentrations, the most serious pollutant and textile wastewater are the most serious problems. Disposal of these wastes into the receiving water damages the environment. Removal of dye wastewater from surface waters is due to not only aesthetic reasons and the effect of dyes on plant photosynthesis and fish mortality in water, but also because many of these dyes are toxic and carcinogenic (1-3).

The basis for the classification of the dye according to chemical structures is the chromophore group, which gives absorption to the dye material. Among these classes are the most known azo dyes. Around 7x10^5 tons of dye are produced annually in the world, and 60-70% of them are azo dyes (4). Most azo dyes, except for some, lead to the formation of aromatic amines that are mutagenic or carcinogenic to human beings. One such class of reactive dyes has complex chemical structures, including organic ring forms with dyed double bonds. A typical case of reactive dyes is the formation of a constant covalent bond between the hydroxyl groups and the dye reactive groups of the cellulose fiber (5). Wastes from reactive dyeing processes require special attention due to their basic properties which relatively low dye fixation ratio, high organic and inorganic substance and high alkalinity (6). It is very difficult to treat wastewater from textile dyeing processes with conventional activated sludge systems. The wastewater color is because the structure of the dyes does not have the biodegradability properties. Physical-chemistry methods such as coagulation/flocculation, clay, perlite and activated carbon adsorption, as well as reverse osmosis systems, have been improved because of removing the color. However, limited success is achieved in these methods and uncompensated costs arise (7). Today, advanced oxidation processes (AOP's) are present for the treatment of wastewaters, such as electro-oxidation, ozonation, photocatalytic degradation, *etc*. (8-10).

Among ozone's numerous applications, decolorization of textile wastewater has gained an increasing interest in the over recent years. AOPs, such as treatment with ozone (O_3), ultra-violet and hydrogen peroxide (UV/H_2O_2, $UV/O_3/H_2O_2$), can prompt to the demolition of the dye-molecule chromophore group, decolorizing thus the textile effluent (11-14).

Ozone is widely used in both drinking and non-drinking water treatment and industrial wastewater treatment. The ozone and its molecular oxygen are the first choice for oxidation or disinfection. Indeed, it is one of the most effective and readily obtainable oxidizing agents that can be produced everywhere. Furthermore, ozone dissociates quickly without leaving any residue, and reactions usually do not produce toxicants.

Ozone reacts, directly or indirectly, with complex organic and inorganic compounds, thereby breaking them into simpler and smaller molecules. The oxidizing action of ozone in aqueous solutions is rather complex since ozone acts by several mechanisms, including the presence of other highly strong oxidizing agents, like atomic oxygen (O), perhydroxyl ($HO_2\bullet$), or hydroxyl ($OH\bullet$) free radicals. In fact, oxidation reactions occur both directly and indirectly. However, the reaction is usually dependent on various factors such as the temperature, pH, and chemical composition of the solution (15-17).

The objective of this study is to demonstrate the ability of ozonation to fully and effectively decolorize aqueous solutions of azo-reactive dye (Reactive Yellow 17 (RY17)). For this purpose, optimum oxidation conditions, e.g. color and Chemical Oxygen Requirement (COD) were removed to determine dye, ozone concentration, pH, and temperature. All of the experiments were applied in the Semi-Batch Bubble Column Reactor (SBBCR).

EXPERIMENTAL

Experimental set-up

The experimental set-up that is shown in Figure 1 consist of oxygen gas, ozone generator, a glass bubble column reactor, reactor, dosimeter, temperature control unit, two peristaltic pumps and two washing bottles. Fischer 502 Model ozone generator was used for the production of ozone from dry oxygen (99.9% purity). All experiments were carried out in a semi-batch bubble column reactor (Diameter: 5 cm, Volume: 2000 mL). Oxygen gas was passed through the ozonizer, where ozone formation takes place. The resulting mixture of O_3 and O_2 was passed through a silicone hose to the bottom of the bubble column in which the dye solution was present. The gas flow rate was controlled by a valve and measured by a flow meter. In all experiments the temperature was kept constant at $20\pm1\ ^{0}C$.

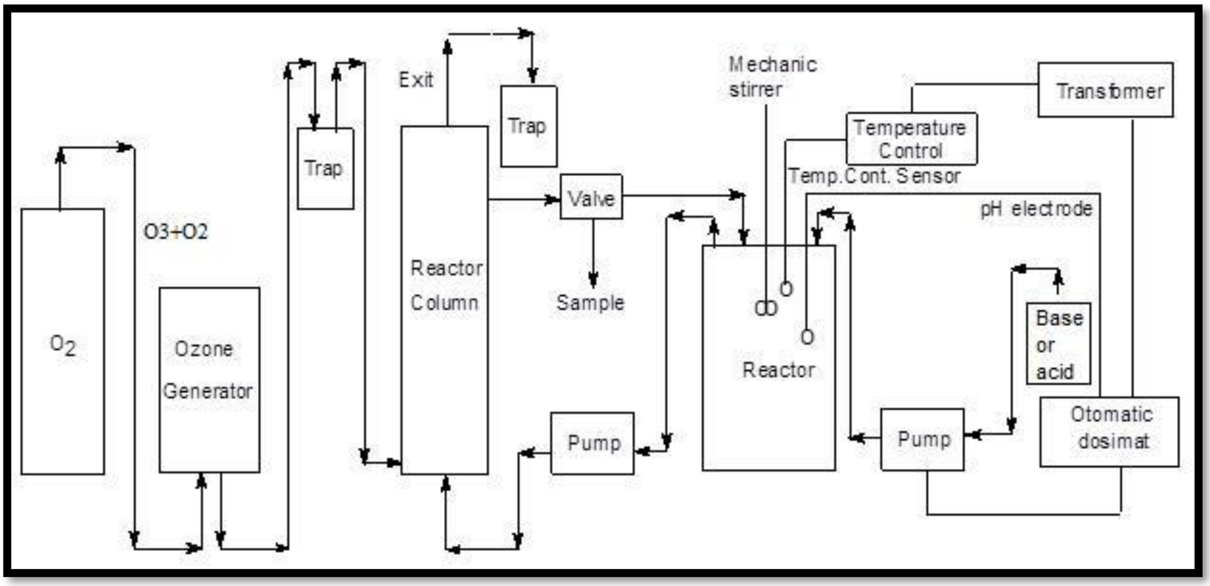

Figure 1. Schematic diagram of the bench-scale reactor system.

Unused ozone was sent to wash bottles containing 2% KI in the bubble column reactor via a silicone hose. The potassium iodide solution was reacted with excess ozone according to the following equation:

$$O_3 + 2\,KI + H_2O \rightarrow I_2 + 2\,KOH + O_2 \qquad \text{(Eq. 1)}$$

The resulting iodine was titrated using standard sodium thiosulfate, in the presence of starch as indicator. The values of unused ozone were determined accordingly. The concentrations of dye solution were determined by Agilent 8453 model spectrophotometer at its maximum absorption wavelength of 408 nm for RY17.

On the basis of our previous experiences, high ozone-air flow rate and high ozone concentration were required for the effective treatment of the dyestuff wastewater by ozone (18-23). Thus, experiments were performed with ozone-air flow rate at 120 L/h.

Reagents and solutions

Due to its widespread use, C.I. Reactive Yellow 17, chosen as the model dyestuff, was purchased from Alfa Aesar. The characteristics of disperse dyes are displayed in Table 1. Figure 2 shows the general structures of the disperse dyes. Dye solutions at a concentration of 1000 mg/L were prepared from distilled water. The pH of the solutions was adjusted by using NaOH (Merck) or H_2SO_4 (Merck) by dosimeter and was measured by using a pH meter (WTW pH 315i). This stock solution was stirred for 30 min. It was then cooled and stored in the dark. The stock solution was used to prepare the desired concentration (100, 200, 300 and 400 mg/L).

Table 1. The characteristics of the reactive dye.

Reactive Dye	Formula	CAS Number	λ_{max} (nm)	Mw (g/mol)
Reactive Yellow 17	$C_{20}H_{20}K_2N_4O_{12}S_3$	20317-19-5	408.0	682.77

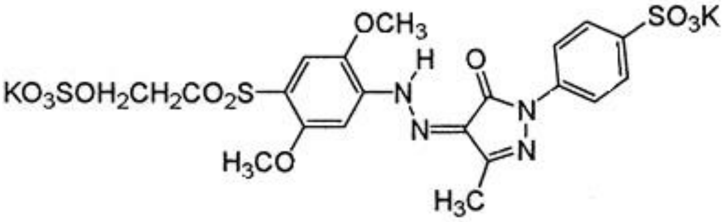

Figure 2. Structures of the Reactive Yellow 17

Equipment

The concentration of each dye solution was determined by an Agilent 8453 model spectrophotometer at maximum absorption wavelength 408.0 nm for RY17. De-ionized water was used throughout the experiments for all solution preparations. The color of dye solutions was measured by an integration method developed COD measurement of Wu *et al*. (1998) and Wu and Wang (2001) (24,25).

This method involved scanning the absorbance of a sample from 200 to 600 nm and integrating the area under the absorbance curve. The integrated area is expressed as the Integrated Absorbance Units (IAU), which is directly proportional to the sample color. The integration method is simpler than the American Dye Manufacturers Institute (ADMI) tristimulus filter method but the two methods have been shown to yield similar results (25,26).

RESULTS AND DISCUSSION

Decolorization kinetics

The reaction mechanisms of ozonation reactions follow two possible pathways of degradation. One of these occurs at basic pH, at which the ozone rapidly forms hydroxyl radical and the other at acidic pH, where ozone reacts directly with organic substrates as an electrophilic. Because ozone attacks the double bonds associated with the color in the dye, it is often used to decolorizing dye wastewaters.

The decomposition of ozone is also influenced by the presence of inorganic/organic species in the reaction medium.

The decolorization of dyes by ozonation is first order with respect to ozone and the dye, respectively (27). If the amount of ozone is increased, the reaction is pseudo-first order according to dye. When the data obtained in this study were calculated it was found that the pseudo first-order reaction.

$$-\frac{dC_{dye}}{dt} = k_{app}.C_{dye} \quad \text{(Eq. 2)}$$

where C_{dye} is dye concentration, and k_{app} is the apparent rate constant.

The representative curve and the corresponding pseudo first-order correlation are shown in Figure 3.

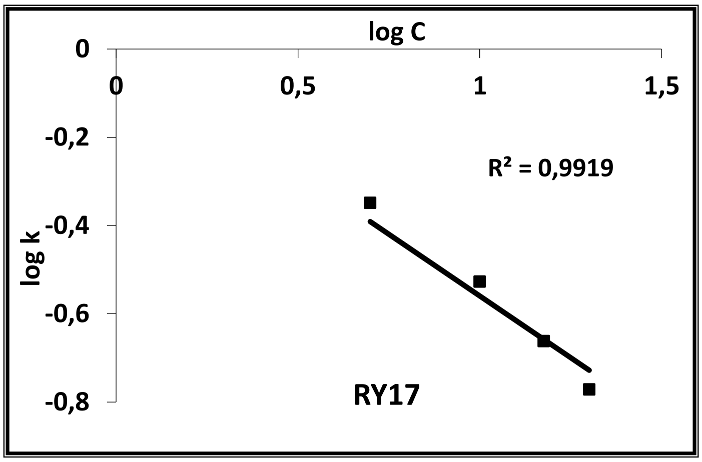

Figure 3. log k = f (log C) plots of RY17.

Also, the apparent rate constant declines logarithmically with the initial dye concentration as follows:

$$k_{app} = 0.8441 \times C_{RY17}^{-0.6955} \qquad \text{(Eq. 3)}$$

where, k_{app} : apparent rate constant, 1/min; C_{dye} : the initial dye concentration, mg/L.

Initial dye concentrations of 5, 10, 15 and 20 mg/L were taken so that the absorbance of the dye solutions can be measured directly without dilution. As can be seen in Table 2, higher values for rate constant could be obtained in a basic medium. For this reason, the pH environment has been chosen to be high for the duration of the study.

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

		k (1/min)			
Reactive dye	**pH**	**C_0 = 5 mg/L**	**C_0 = 10 mg/L**	**C_0 = 15 mg/L**	**C_0 = 20 mg/L**
Reactive Yellow 17	6.0	0.278	0.202	0.145	0.092
	8.0	0.404	0.338	0.246	0.113
	10.0	0.411	0.317	0.208	0.106
	12.0	**0.448**	**0.246**	**0.187**	**0.099**

The effect of pH of initial solution on COD

At the beginning of the ozonation process, the solution (5 L) of dye that has 300 mg/L concentration was put into the reactor. The experiment was initiated by the formation of ozone gas. Sampling was done at regular intervals to determine dye concentration and COD. The pH of the RY17 wastewater prior to reaction with ozone was determined to be 6.3. The COD of reactive dyestuff wastewaters was reduced from 761 mg/L to 541 mg/L after ozone treatment for 2 hrs. When the pH was adjusted to 12.0, the COD value of the reactive dye solution was reduced to 163 mg/L. With the idea that the difference in the results came from the difference of the pH of samples, ozone treatment experiments were performed with various pH of samples. For this purpose, COD values were measured at selected pH ranges of 2-12 after ozone treatment and the results are shown in Figure 4. The results obtained with RY17 wastewater showed that the COD reduction was significant at pH 12. For this reason, 12 was chosen as the most suitable pH value for subsequent experiments.

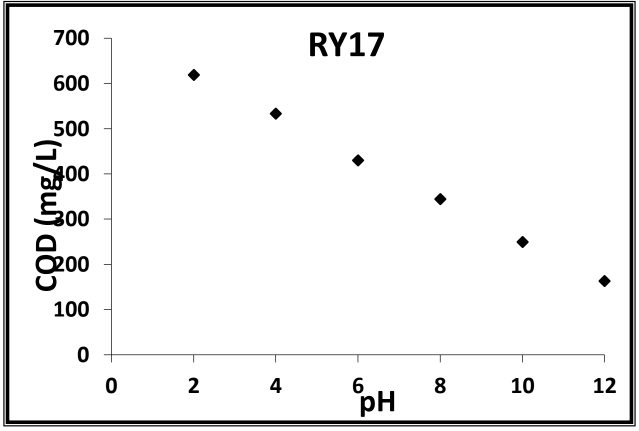

Figure 4. Effect of pH of the initial solution on COD (COD raw reactive dyestuff: 761 mg/L for DY17; Ozone conc.: 24 g/m^3; Dye concentration: 300 mg/L; Dye solution: 5 L; Ozone-air flow rate: 120 L/h; Ozonation time: 120 min.).

Spectrophotometric investigation of the process

The decolorization UV-Vis spectra of RY17 is shown in Figure 5. During the course of the 12-minute reaction period, the absorption of RY17 in solution decreased with the duration of the reaction. In the presence of ozone, the decrease in absorbance at 408.0 nm of the RY17 solution showed that the RY17 structure was reduced or abolished.

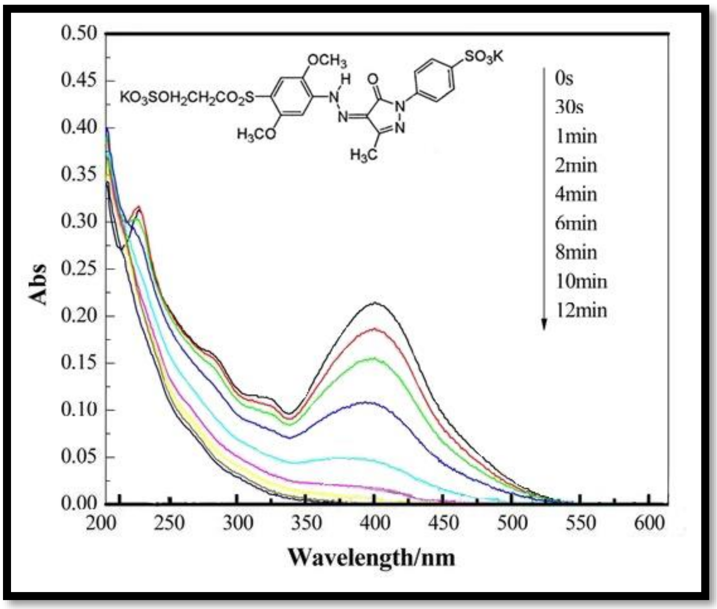

Figure 5. UV–Vis spectral changes of RY17 (300 mg/L) with ozone after different reaction time at initial pH.

Effect of reaction time

COD was also measured during the reaction. As shown in Figure 6, the optimal time for 120 minutes of ozonation was chosen because there was no reasonable reduction in the COD of the dye solution after 120 minutes of ozonation. Figure 6 shows that COD of dye wastewater decreases 78.58% for RY17 (at pH 12.0) with ozonation.

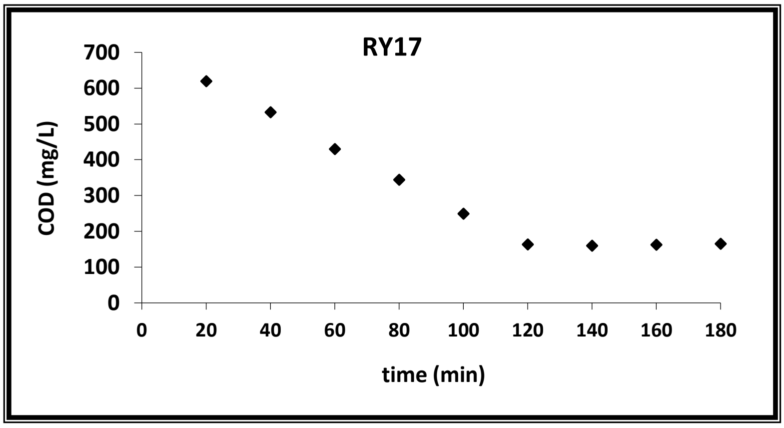

Figure 6. CODs of RY17 with ozone after different reaction time at pH 12. (Ozone conc.: 24 g/m^3; Dye concentration: 300 mg/L; Dye solution: 5 L; Ozone-air flow rate: 120 L/h).

Effect of initial dye concentration on rate of dye removal

Figure 7 shows the change in the dye concentration during the ozonation at different initial concentrations. Based to these results, the removal rate of RY17 is higher at lower initial dye concentrations and lower at higher dye concentrations.

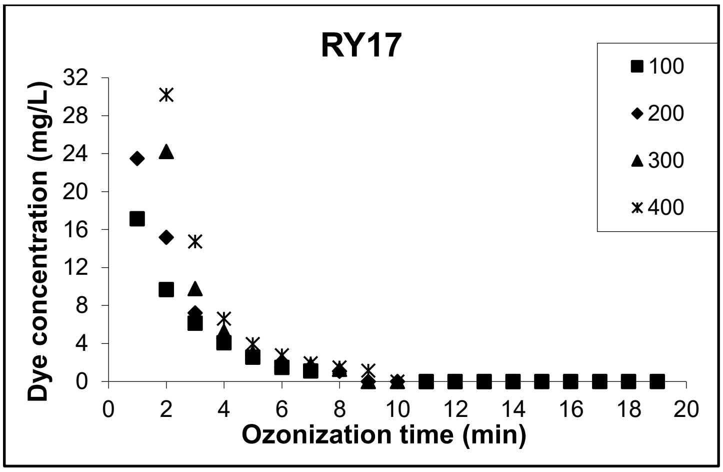

Figure 7. Concentration-time data for different dye concentration treated with ozone (Ozone conc.: 24 g/m^3; Dye solution: 5 L; Ozone-air flow rate: 120 L/h; pH:12)

Effect of initial dye concentration on decolorization time

Figure 8 shows the effect of initial dye concentrations (100 to 400 mg/L) on the time required for the decolorization process. According to the results obtained, the color removal time is directly proportional to the initial dye concentration. The data fit equation:

$$t_D = m.c \quad \text{(Eq. 4)}$$

where t_D is the dye decolorization time (min), m: a constant, and c: the initial dye concentration (mg/L).

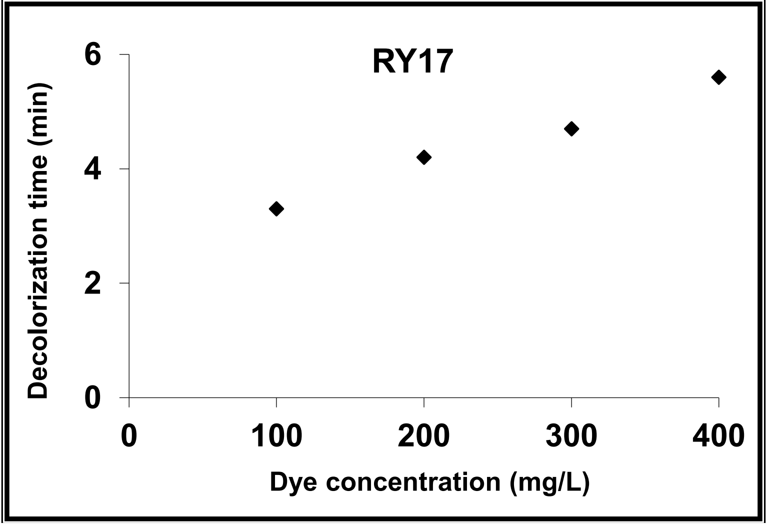

Figure 8. Effect of initial dye concentration on the decolorization time of RY17 or dye treated by ozone (Ozone conc.: 24 g/m^3; Dye solution: 5 L; Ozone-air flow rate: 120 L/h; pH: 12).

Effect of ozone concentration on decolorization time

Figure 9 shows the relationship between ozone concentration and the duration of decolorization; with increasing ozone concentration, it is very clear that the duration of color removal decreases linearly. For example, increasing ozone concentration from 4.21 g/m^3 to 24.03 g/m^3 in the gas phase reduces the decolorization time of 300 mg/L dye concentration by 73.08%. This result is consistent with mass transfer theory (28). According to this theory, the repulsive force required to transfer the ozone to the dye solution, in other words, increases as the concentration of ozone in the air bubbles (ozone carrier), the rate of dye oxidation increases.

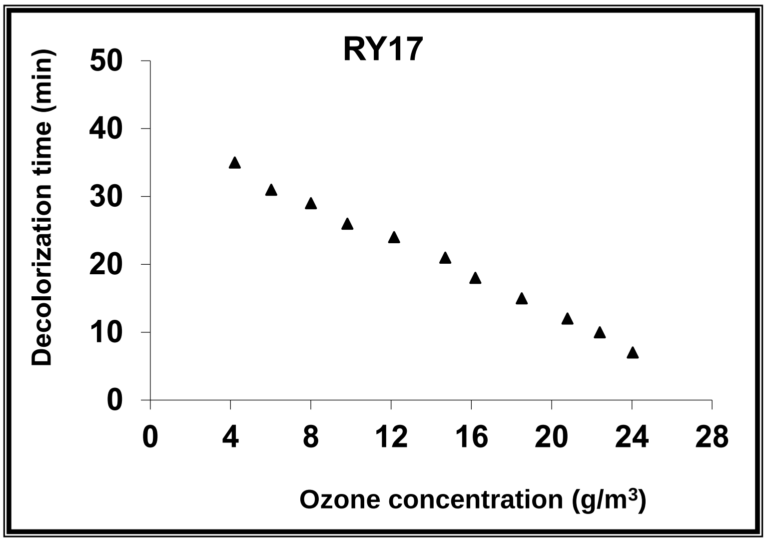

Figure 9. Effect of ozone concentration on dye decolorization time (Dye conc.: 300 mg/L; Dye solution: 5 L; Ozone-air flow rate: 120 L/h; pH: 12).

Effect of pH of initial dye solution on decolorization time

Figure 10 shows the initial dye solution pH versus decolorization time of the dye solution. It appears that the decolorization time decreases with increasing initial pH of the solution. The rate of decomposition of ozone is directed toward the formation of hydroxyl radicals by increasing pH. This explains the reduction of 67.10% of the dye decolorization time by increasing the pH from 2 to 12.

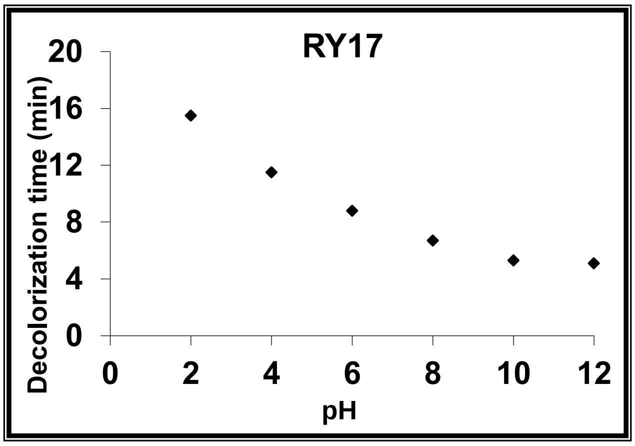

Figure 10. Effect of initial dye solution pH on decolorization time (Dye conc.: 300 mg/L; Dye solution: 5 L; Ozone-air flow rate: 120 L/h; Ozone conc.: 24 g/m^3)

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CONCLUSIONS

In this study, the aqueous solutions of Reactive Yellow 17, selected as the model textile dye, were ozonated in a semi-batch bubble column reactor. To increase the solubility of the aqueous solutions of the stubborn pollutant at the laboratory scale, an experimental series of experiments was conducted to evaluate the effectiveness of the indirect ozonation of the radical type reactions with the RY17 model. A detailed review of the results provided us with the following results:

After ozone bubbling treatment, the reactive dye wastewater showed a 78.58% reduction in COD. The results obtained with reactive dye (RY17) showed that COD reduction and decolorization were more effective under basic conditions. The decolorization took place in 12 minutes for RY17, ozone consumption continued for another 30 minutes, after which a large part of the degradation was completed. A large number of bubbly ozone gases at high concentrations have been effective in reducing COD at high inlet gas flow-rates. In all experimental studies, decomposition kinetics for the reaction of the ozone-dye solution were observed as pseudo-first order. The increase in k by the increase of the ozone dose can be explained by the higher ozone dose applied to increase the dissolved ozone concentration. This makes decolorization of the dye solution faster. Higher rate constants were obtained at higher pH values in the experiments. This can be explained by the fact that high pH values promote spontaneous dissociation of ozone in the water.

The knowledge gained in this study is thought to be a guide for future studies. However, it is highly probable that UV-assisted ozonation, which is to be carried out as a continuation of these studies, may have a higher effect. This laboratory-scale work can be used in industrial treatment systems. The industrialists do not prefer ozonation because of its expensiveness, but they should be aware of its benefit for ecosystem. Although they seem cheap, the damage of the systems used as alternatives in the removal and disintegration of the aromatic compounds in particular, must not be ignored. However, it should be remembered that the degradation products in the purification process may be more harmful. For this reason, the continuity of such studies will provide an idea for the plant as well as a pre-feasibility.

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