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Decolorization of textile basic dye in aqueous solution by ozone

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ABSTRACT

In this study, the factors affecting the rate of chemical oxygen demand (COD) of a synthetic waste solution containing a water soluble basic dye [Methylene Blue] were investigated. Decolorization of the dye was achieved by ozonation. The research was conducted using a batch bubble column to take the advantage of the intensive back-mixing that prevails in bubble columns. As a result, the COD of basic dyestuff wastewater was reduced to 64.96% and decolorization was observed under basic conditions (pH 12), complete MB degradation occurring in 12 min. Ozone consumption continued for a further 16 min after which time most of the degradation reactions were complete. Kinetic studies showed that direct ozonation of the aqueous dyes represented a pseudo-first-order reaction with respect to the dye. The apparent rate constant, which increased with both the applied ozone dose and higher pH values, declined logarithmically with the initial dye concentration.

1. Introduction

Dyes and pigments have been utilized for coloring in the textile industry for many years [1]. Several types of textile dyes are available for use with various types of textile materials. Among these many types, 'cationic dyes', commonly known as basic dyes, are widely used in acrylic, nylon, silk, and wool dyeing [2].

Textile industries are responsible for the discharge of large quantities of dyes into natural waterways due to inefficiencies in dyeing techniques. Up to 50% of dyes may be lost directly into waterways when using reactive dyes [3]. The presence of dyes in the effluent even at very low concentrations could highly be visible and undesirable [4]. Colored wastewater damages the esthetic nature of water and reduces light penetration through the water's surface, and also the photosynthetic activity of aquatic organisms. Textile wastewaters containing toxic and potential carcinogenic substances must be adequately treated before they can discharge into receiving water bodies [5].

There are several applied treatment methods for textile effluents, involving biological, physical or chemical methods and combinations of these. Since dyes were intentionally designed to resist degradation, conventional biological wastewater treatment methods are ineffective in removing the color [6]. Ozone is very effective in decolorizing textile effluents. The decomposition rate of ozone is affected by pH and initial dye concentration. 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. Ozone is frequently used for decolorizing dye wastewaters because it attacks conjugated double bonds which are often associated with color. Ozone decomposition is also affected by the presence of inorganic/organic species in the reaction medium.

In this study, a synthetic waste solution containing the water soluble basic dye MB was ozonated and the factors affecting the rate of chemical oxygen demand were investigated. The research was conducted using a batch bubble column to take the advantage of the intensive back-mixing that prevails in such columns.

2. Materials and methods

2.1. Experimental set-up

The experimental set-up that is shown in Fig. 1 consists of oxygen gas, ozone generator, a glass bubble column reactor and two washing bottles. A Fischer 502 ozone generator was used for the production of ozone from dry oxygen (99.9% purity). The reactor had a glass column of 5 cm diameter and 110 cm height with sintered glass at the bottom through which ozone was introduced

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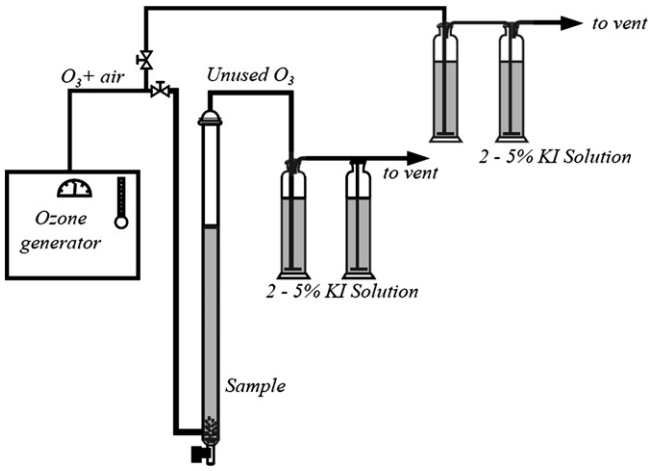

Fig. 1. Schematic diagram of the bench-scale reactor system.

into the solution. The reactor was followed by two washing bottles, each of them containing 500 mL of acidified 2–5% KI solution for determining unused ozone. The bubble column reactor was filled with 2000 mL of dye solution before each run. Oxygen gas was allowed to pass through the ozonizer where ozone formation takes place. The outlet stream from the ozonizer containing O_3 and O_2 mixture was allowed to pass through Tygon tubing connected to the bottom of the bubble column. The gas flow rate was controlled by a needle valve and was measured by air flow meters. The temperature was fixed at 20 ± 1 °C during all experiments. The pH of wastewater was adjusted to the desired level with Merck quality analytical grade 0.1 N NaOH and H_2SO_4.

The unused ozone was taken out of the bubble column reactor through the Tygon tubing, and bubbled into 2% KI solution in the washing bottles, where the potassium iodide solution reacted with the excess ozone according to the following equation:

$$O_3 + 2KI + H_2O \rightarrow I_2 + 2KOH + O_2 \quad (1)$$

The resulting iodine was titrated using standard sodium thiosulfate, in the presence of starch as indicator. The values of unused ozone were determined, according to the procedure given by our previous studies [7–9].

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. Thus, experiments were performed with an ozone-air flow rate at 120 L/h with a 2000 mL sample volume and an output current of 2.5 A.

2.2. Reagents and solutions

The dye named commercially Basic Blue 9 [Methylene Blue (MB)]; CI 52015; ($C_{16}H_{18}N_3SCl$) (3,7-bis(dimethylamino) phenolthiazin-5-ium chloride; purity of the dye:100%) was purchased from

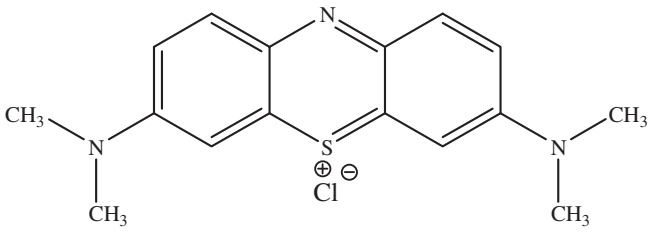

Fig. 2. Structure of MB.

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

Basic 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
Methylene Blue	6.0	0.162	0.144	0.135	0.128
	8.0	0.218	0.191	0.168	0.149
	10.0	0.326	0.264	0.212	0.168
	12.0	0.503	0.342	0.246	0.200

Dystar. It is water-soluble (MW: 319.85 g/mol) and has the structure as shown in Fig. 2.

2.3. Equipment

The concentrations of dye solutions were determined by an Agilent 8453 model spectrophotometer at its maximum absorption wavelength 665 nm for MB. COD measurement was carried out according to the Standard Methods [10].

3. Results and discussion

3.1. Decolorization kinetics

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 [11]. 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.

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 ($\ln C = -k \cdot t + \text{const}$) transformed into Equation (2) [12–15]:

$$k \cdot t = \ln(C_0 - C) \quad (2)$$

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, 2009) 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 [8,9,15,16].

Equation (2) was used in the form of $C = C_0 \cdot e^{-kt}$, 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 dye studied are given in Table 1.

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 Fig. 3.

Similarly, the results obtained previously with wastewater containing a basic dye [16], the apparent rate constant (k_{app}) declined logarithmically with the initial dye concentration as in Equation (3).

$$k_{app} = 0.179 \times C_{dye}^{-0.6674} \quad (3)$$

where,

k_{app}: apparent rate constant, 1/min

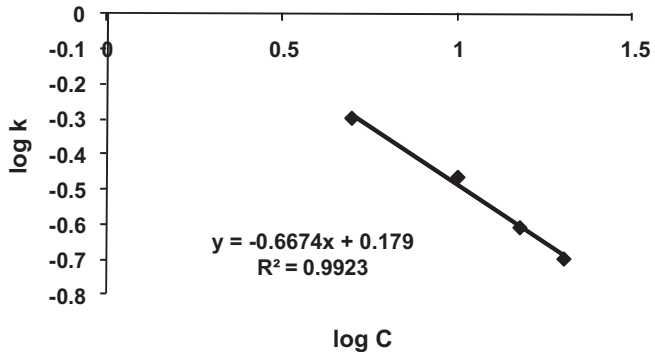

Fig. 3. log $k = f$ (log C) plots of MB.

C_{dye}: the initial dye concentration, mg/L.

As can be seen in Table 1, higher values for the rate constant could be obtained at basic pH. Therefore, a basic pH medium was selected for further experiments.

3.2. The effect of pH of initial solution on COD

At the beginning of the ozonation process, 2000 mL MB solution at a concentration of 400 mg/L concentration was added into the reactor. Experiments were started immediately after the admission of ozone gas. Samples were taken at regular time intervals for the determination of MB concentration and COD at the sample port.

The pH of raw direct dyestuff wastewater was 6.5. The COD of direct dyestuff wastewater was reduced from 1136 mg/L to 871 mg/L after ozone bubbling treatment for 2 h The COD of direct dyestuff wastewater was reduced to 398 mg/L when the pH was changed to 12.0. Since the differences in the results may arise from the difference of the pH values of the samples, ozone treatment experiments were performed with samples in various pH. The COD after ozone treatment was measured at the various pH values in the range of 2–12, and the results are shown in Fig. 4. The results with the direct dyestuff wastewater showed that COD reduction was noticeable under basic conditions at pH 12. Thus, pH 12 was chosen as optimum for subsequent experiments.

3.3. Spectrophotometric investigation of process

The decolorization of the MB component is shown in Fig. 5. During the progress of the 28 min reaction time, the absorption intensity of the MB component in solution became weaker with reaction time. This phenomenon indicated that MB molecules were degraded and removed in the presence of ozone.

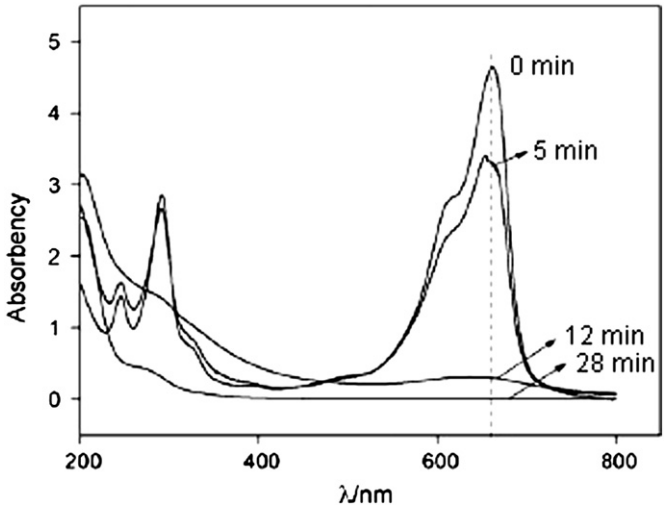

Fig. 5. UV–Vis spectra changes of MB (400 mg/L) with ozone after different reaction time at initial pH.

The decrease of the absorption peak of MB solution at $\lambda_{max} = 665$ nm indicated a rapid degradation of the MB component in the solution.

Ozone treatment showed a limited mineralization of the organic compounds concerning the removal of micro pollutants in the dye solution. The high color removal efficiency but low Chemical Oxygen Demand (COD) illustrates that only chromophores were destructed and reduced instead of completely oxidizing the organic pollutants to CO_2 and H_2O. In the aspect of COD reduction, catalytic processes showed higher effect. As mentioned above, although the ozone process alone has the ability to produce hydroxyl radicals via the decomposition pathway of radical-type chained reactions, the net production efficiency of free radicals was still less than that of catalytic ozonation process according to our previous studies.

3.4. Effect of reaction time

COD was also measured during the reaction. Fig. 6 shows that after a reaction of 120 min, the COD of dye wastewater was 64.96% with ozonation at pH 12.0.

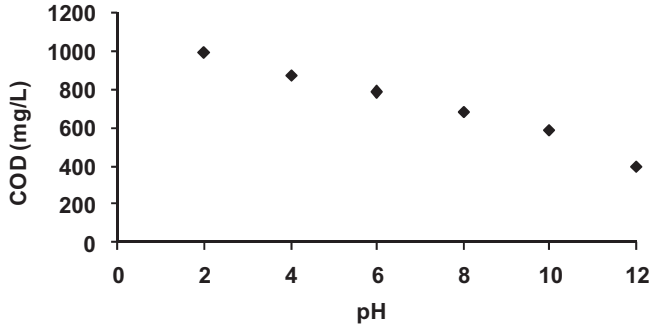

Fig. 4. Effect of pH of the initial solution on COD (COD raw basic dyestuff: 1136 mg/L; COD environmental standard: 150 mg/L; Ozone conc.: 24 g/m^3; Dye concentration: 400 mg/L; Dye solution: 2000 mL; Ozone-air flow rate: 120 L/h; Ozonation time: 120 min).

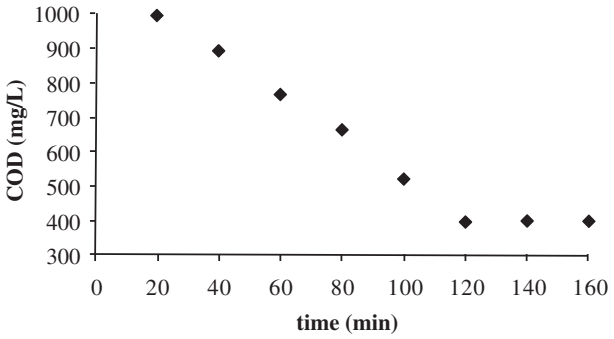

Fig. 6. COD of MB with ozone after different reaction time at pH 12 (Ozone conc.: 24 g/m^3; Dye concentration: 400 mg/L; Dye solution: 2000 mL; Ozone-air flow rate: 120 L/h).

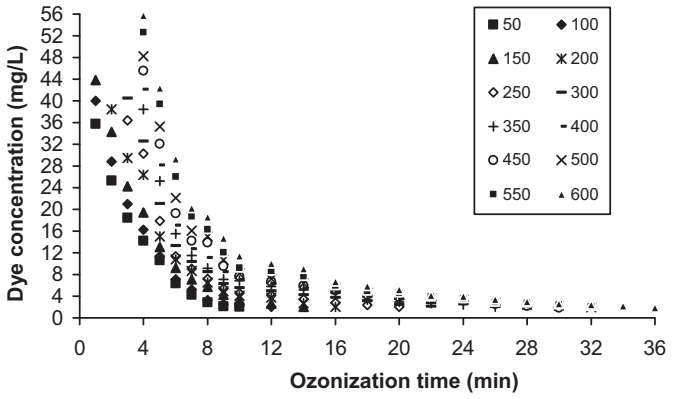

Fig. 7. Concentration time data for different MB concentration treated with ozone (Ozone conc.: 24 g/m^3; Dye solution: 2000 mL; Ozone-air flow rate: 120 L/h; pH: 12).

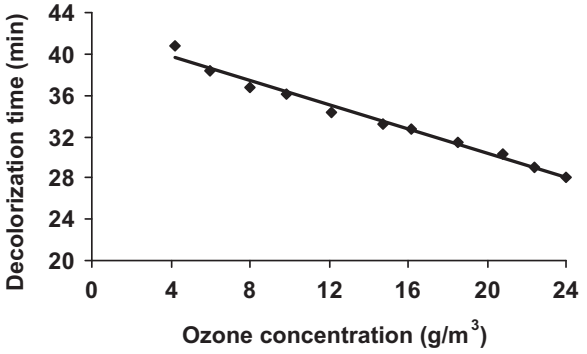

Fig. 9. Effect of ozone concentration on dye decolorization time (Dye conc.: 400 mg/L; Dye solution: 2000 mL; Ozone-air flow rate: 120 L/h; pH: 12).

3.5. Effect of initial dye concentration on rate of dye removal

Fig. 7 shows the change of dye concentration with time during ozonation at different initial dye concentrations. The rate of dye removal was high at the beginning and decreases with time.

3.6. Effect of initial dye concentration on decolorization time

Fig. 8 shows the effect of initial basic dye concentrations (50–600 mg/L) on the time required for the decolorization process. The decolorization time increases with increasing initial dye concentration in the waste. The data fit the equation:

$$t_D = m \cdot c$$

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

3.7. Effect of ozone concentration on decolorization time

Fig. 9 shows the effect of ozone concentration on the decolorization time. It is very clear that the decolorization time decreases linearly with the increase in ozone concentration. 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 400 mg/L dye concentration by about 88.43%. This result is consistent with the theories of mass transfer [17]. According to these theories, as the ozone concentration increases in the air bubbles, the driving force for the transfer of ozone to the dye solution increases with a consequent increase in ozone concentration in the solution and rate of dye oxidation.

A large amount of bubbles was formed at high inlet gas flow rates. High ozone concentrations were effective for the reduction of COD.

3.8. Effect of pH of initial dye solution on decolorization time

Fig. 10 shows the effect of varying the pH of the initial dye solution on the dye decolorization time. It can be seen that the decolorization time decreases with increasing pH of the initial solution. According to Elovitz and von Gunten, the pH affects the ozonation process by affecting the rate of ozone decomposition and ozonation kinetics [18]. The rate of ozone decomposition is favored by the formation of hydroxyl radicals at higher pH values. This explains the reduction of dye decolorization time to 59.62% when the pH value was altered from 2 to 12.

The color of the dyestuff arises mainly from the aromatic π-system. Ozone is an excellent agent in the decomposition of aromatic covalent compounds, and hence it is good for the decolorization of the dyestuff wastewater [19,20].

Raw dyestuff wastewater samples had dark blue color before the treatment. Direct dyestuff wastewater was remarkably decolorized with ozone treatment. A transparent yellow color was observed after about 12 min of reaction. Decolorization was completed in

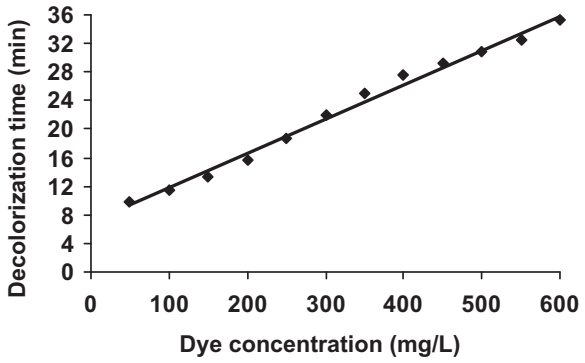

Fig. 8. Effect of initial dye concentration on the decolorization time of MB dye treated by ozone (Ozone conc.: 24 g/m^3; Dye solution: 2000 mL; Ozone-air flow rate: 120 L/h; pH: 12).

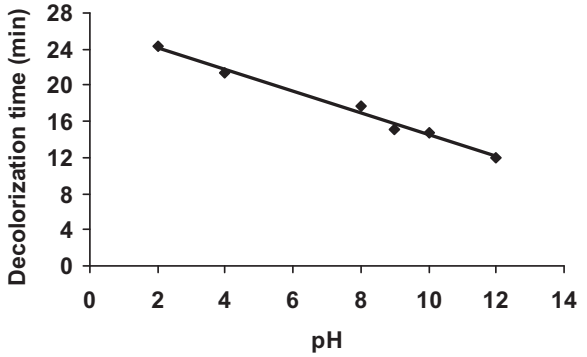

Fig. 10. Effect of initial solution pH on decolorization time (Dye conc.: 400 mg/L; Dye solution: 2000 mL; Ozone-air flow rate: 120 L/h; Ozone conc.: 24 g/m^3).

about 28 min. The reduction of the absorbance of the direct dyestuff wastewater was 94.56% after 28 min of reaction.

4. Conclusions

In this study, the aqueous solution of a model basic textile dye, MB, was ozonated in a batch reactor. An experimental investigation was carried out to evaluate the effectiveness of indirect ozonation occurring by radical-type reactions for enhancing the degradability of aqueous solutions of the model recalcitrant pollutant on a laboratory scale. A detailed examination of the results allows us to draw the following conclusions:

It was shown that the COD of basic dyestuff wastewater was reduced 64.96% after ozone bubbling treatment. The results with the basic dye showed that COD reduction and decolorization were remarkable under basic conditions (pH 12). A large amount of bubbles was formed at high inlet gas flow rates. High ozone concentration was effective for the reduction of COD. Decolorization kinetics Pseudo-first-order trends for the ozone–dye reaction were observed in all of the experimental runs. The explanation for the increase of k with the applied ozone dose, is that higher applied ozone dose increased the dissolved ozone concentration, C_{ozone}, which makes the decolorization faster; while higher pH values resulted in larger rate constant This could be explained by the fact that high pH values promote the self-decomposition of ozone in water.

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