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Decolorization of aqueous textile reactive dye by ozone

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Abstract

The aqueous solution of a model textile reactive dye, C.I. Reactive Blue 15, was ozonated in a semi-batch reactor. Results of kinetic study showed that ozonation of the aqueous reactive dye was a pseudo-first-order reaction with respect to the dye. The apparent rate constant increased with both the applied ozone dose and temperature, but declined logarithmically with initial dye concentration. It was also found that the volumetric mass transfer coefficient of ozone increased linearly with initial dye concentration, applied ozone dose and temperature, respectively. The experimental data further indicated that ozonation effectively removed chemical oxygen demand (COD) and enhanced the biodegradability of the aqueous dye solutions.

Keywords: Textile reactive dye; Ozone; Color removal; Wastewater treatment; Ozone mass transfer

1. Introduction

Textile effluents are characterized by heavy color resulting from dyes remaining in the water. Colored wastewater not only affects the aesthetic merit and water transparency of receiving waterbodies [1,2], but there are also environmental concerns about the possible toxicity and carcinogenicity of some organic dyes. In the case of reactive dyes commonly used for cotton dyeing, the quality of the wastewater is further degraded because around 30% of the dyes applied remain in the effluents [3–6]. Since dyes were intentionally designed to resist degradation, conventional biological wastewater treatment methods are ineffective in removing the color [1,2,5,7–9].

Ozone is very effective in decolorizing textile effluents [4,6]. Ozone can also convert biorefractory dyes in wastewater into biodegradable species so that effective biological treatment can follow [3,10,11]. It has been reported that the rate-limiting step in the ozonation of dye-containing wastewater is the mass transfer of ozone from the gas-phase to the liquid-phase [12–15]. However, the driving force for ozone mass transfer, i.e., the difference between the concentration of the dissolved ozone and the equilibrium ozone concentration at the gas–liquid interface, varies with water quality parameters and operating conditions [10,16]. Consequently, the efficacy of ozone treatment of textile wastewater depends on water quality parameters such as the characteristics of the dye, concentration of the dye, etc. It also depends on operating parameters such as the applied ozone dose and temperature.

In this study, the aqueous solution of a model textile reactive dye, C.I. Reactive Blue 15, was ozonated in a semi-batch reactor. Experiments were designed to quantify the effects of several water-quality and operating parameters on the decolorization of this representative system. The extent of biodegradability increased after ozonation for this system was also investigated.

2. Experimental

2.1. Materials and methods

C.I. Reactive Blue 15 was purchased from Sigma–Aldrich Canada (Oakville, Ontario). All other chemicals used were reagent grade and obtained from Sigma–Aldrich or BDH Inc. (Toronto, Ontario). Chemical oxygen demand (COD) vials and biological oxygen demand (BOD) bottles were all supplied by VWR Canlab (Mississauga, Ontario).

The color of the aqueous dye solutions were measured by an integration method developed previously [6,10]. This method involved scanning the absorbance of a sample from 400 to 700 nm (Beckman DU 650 spectrophotometer, Beckman Instruments Canada Inc., Mississauga, Ontario) and integrat-

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ing the area under the absorbance curve. This 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 Manufactures Institute (ADMI) tristimulus filter method but the two methods have been shown to yield similar results [6,17].

The dissolved ozone concentration was measured by the indigo method [17]. The 5-day BOD (BOD_5) and COD of the samples were all measured by standard methods [17].

2.2. Apparatus and procedure of ozonation

Ozone was generated from pure oxygen by a Model GL-1 ozone generator (PCI-WEDECO Environmental Technologies, Charlotte, NC). The concentration of ozone in the output gas of the ozone generator was measured by an ozone monitor (Model HC-400) from the same company. The applied ozone dose could be readily adjustable by varying ozone weight percentage and/or gas flowrate. In this study it was adjusted by varying ozone weight percentage while keeping the gas flowrate and pressure constant. The ozone weight percentages examined were 1.0, 1.5, 2.0, 2.5 and 4.0%, respectively. The reactor was a 500 mL gas washing bottle equipped with a porous gas diffuser (VWR Canlab, Mississauga, Ontario). Excess ozone leaving the reactor was destroyed by a catalytic ozone-destruct unit filled with Carulite catalyst (Carus Chemical Company, Peru, IL). More details were described elsewhere [6,10].

The aqueous dye solution was prepared by dissolving C.I. Reactive Blue 15 in distilled, deionized water. The dye concentration of the dye solution varied to simulate those dye concentrations found in residual dyebaths and diluted effluents [6].

The ozonation process started when the ozone–oxygen mixture from the ozone generator was sparged into the reactor, which was operated in semi-batch mode by feeding the ozone-containing gas continuously. The operating pressure was 82.73 kPa (12 psi). Samples were taken at appropriate time intervals to analyze color and concentration of dissolved ozone, respectively. The BOD_5 and COD of the samples were measured before and after 30 min ozonation.

3. Results and discussion

3.1. Decolorization kinetics

For the decolorization of Reactive Blue 15, the first-order behavior with respect to the dye concentration was observed in all experimental runs:

$$-\frac{dC_{dye}}{dt} = kC_{dye} \tag{1}$$

where C_{dye} is the concentration of the dye and k is the apparent rate constant. This observation is in agreement with previous reports involving ozonation of aqueous organic chemicals. The apparent rate constant k is the product of dissolved ozone concentration, C_{ozone}, and the intrinsic rate constant [10,12,13,18,19,20].

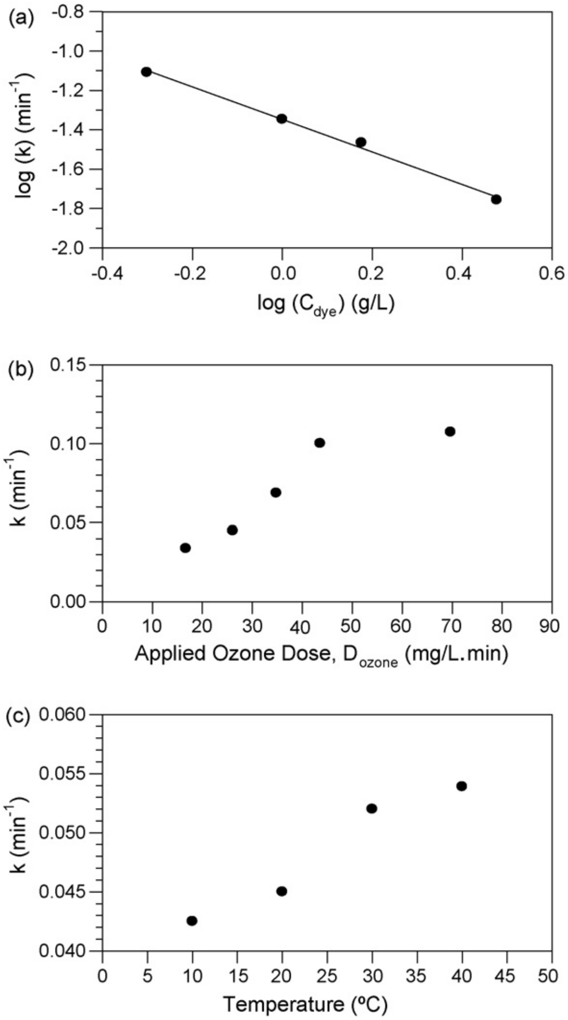

Fig. 1. Dependence of the apparent rate constant of decolorization k on initial dye concentration, applied ozone dose and temperature. (a) $D_{ozone} = 26.1$ mg/L min, $T = 20\,°C$. (b) $C_{dye} = 1.0$ g/L, $T = 20\,°C$. (c) $C_{dye} = 1.0$ g/L, $D_{ozone} = 26.1$ mg/L min.

Fig. 1 shows the variation of k with initial dye concentration, applied ozone dose (D_{ozone}) and temperature. It is observed from Fig. 1 that k increases with the applied ozone dose and temperature, but declines logarithmically with initial dye concentration.

According to Fig. 1, k declines logarithmically with the initial dye concentration as:

$$k = 0.045C_{dye}^{-0.8258} \tag{2}$$

where the units of k and C_{dye} are min^{-1} and g/L, respectively. The fact that k varied with the initial dye concentration at a constant temperature further confirmed that it is an apparent rate constant instead of a real one, because the latter is the function of temperature only [19]. The decrease in k could be attributed to the generation of more intermediates with the increase in C_{dye}. These intermediates consumed more ozone, and C_{ozone} was thus lower with the higher initial dye concentration. Consequently, the apparent rate constant declined with $C_{dye.}$ The logarithmic relationship between the apparent rate constant and the initial dye concentration derived in this study is in agreement qualitatively with that observed in our previous study on a textile wastewater system containing more than one reactive dye and a number of proprietary auxiliary ingredients [6]. The linear log(k)–log(C_{dye}) relationships observed from the two systems of different compositions indicate that the linearity between log(k) and log(C_{dye}) seems valid for the ozonation of reactive dyes regardless of the co-existence of other compounds. Revelation of such linearity makes it possible to predict the rate constant from the initial dye concentration, provided that this relationship is further verified by testing more textile wastewater systems.

For the increase of k with the applied ozone dose and temperature observed in Fig. 1, the explanations are that higher applied ozone dose increased the dissolved ozone concentration, C_{ozone}, which makes the decolorization faster; while higher temperature resulted in larger rate constant according to the Arrhenius equation [19].

3.2. Ozone mass transfer

In a completely mixed semi-batch reactor with no chemical reaction, the mass balance of ozone is expressed as [21]:

$$\frac{dC_{\text{ozone}}}{dt} = k_L^o a(C^* - C_{\text{ozone}}) - r \tag{3}$$

where C^* is the equilibrium ozone concentration at the gas–liquid interface, $k_L^o a$ is the physical volumetric mass transfer coefficient of ozone [21], and r is the rate of ozone self-decomposition. In a solution of low pH, the rate of ozone decomposition is negligible [22]. By neglecting ozone self-decomposition and integrating Eq. (3) from $C_{\text{ozone}} = 0$ at $t = 0$ to $C_{\text{ozone}} = C_{\text{ozone}}$ at $t = t$ yields

$$\ln(C^* - C_{\text{ozone}}) = -k_L^o a t + \ln C^* \tag{4}$$

Values of $k_L^o a$ can be obtained by plotting the left-hand side of Eq. (4) versus the ozonation time, t. For the values of C^*, they were determined when the concentrations of dissolved ozone stop changing with the gas–liquid contact time.

The dye solutions were ozonated to examine the dependence of the rate of ozone mass transfer on initial dye concentration, applied ozone dose, and temperature. The applied ozone dose was adjusted by changing the ozone weight percentage in the gas mixture while maintaining the gas flowrate at 0.52 L/min and pressure at 82.73 kPa (12 psi). During ozonation, the color of the dye solutions decreased with the time whereas the concentration of the dissolved ozone initially increased with the time, but it would soon reach an equilibrium. The representative profiles can be found in Fig. 2.

When dye solutions instead of organic-free water were ozonated, the adsorption of ozone into water was enhanced. The enhancement factor, E, is the ratio of the amount absorbed into a quiescent liquid in a given time when reaction occurs to the amount absorbed in the same time in the absence of reaction [23]. By measuring the ozone absorption rates in the presence and absence of chemical reactions, respectively, the values of E can be obtained. Applying the following

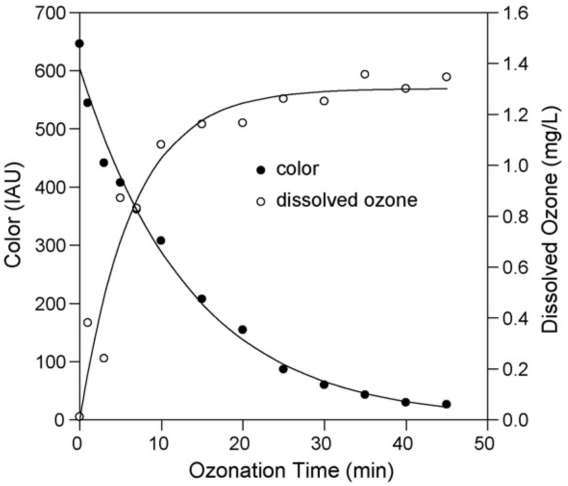

Fig. 2. Color and dissolved ozone concentration of the aqueous dye solution as functions of ozonation time (initial dye concentration = 1.0 g/L, applied ozone dose = 26.1 mg/L min, T = 20 °C).

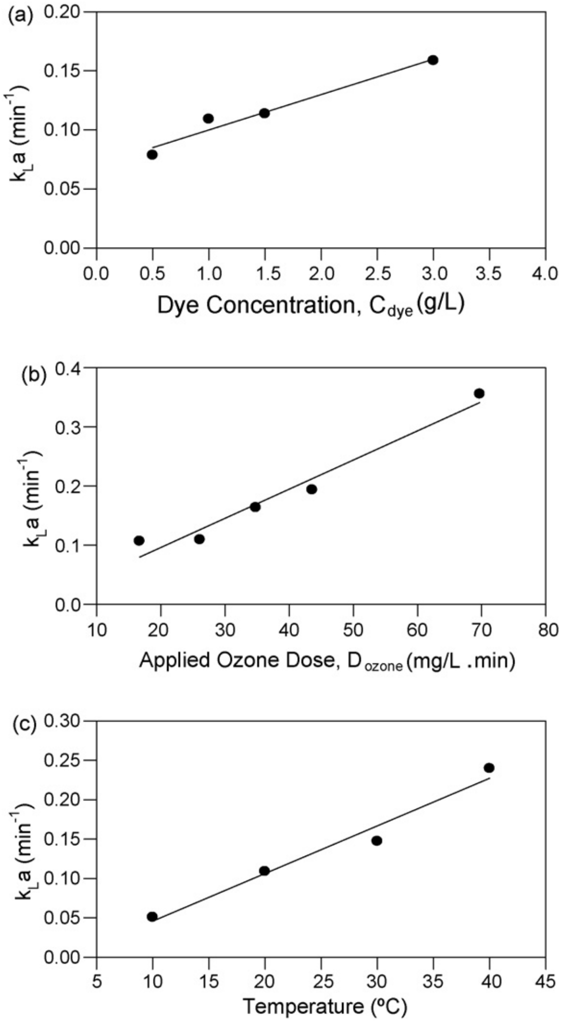

Fig. 3. Dependence of the volumetric mass transfer coefficient of ozone on initial dye concentration, applied ozone dose and temperature. (a) D_{ozone} = 26.1 mg/L min, T = 20 °C. (b) C_{dye} = 1.0 g/L, T = 20 °C. (c) C_{dye} = 1.0 g/L, D_{ozone} = 26.1 mg/L min.

Table 1
COD removal and biodegradability increase of Reactive Blue 15 after 30 min ozonation (gas flowrate = 0.52 L/min, gas pressure = 82.73 kPa (12 psi))

	$(COD)_0$[a] (mg/L)	$(COD)_{30}$[a] (mg/L)	COD removal (%)	$(BOD_5)_0$[b] (mg/L)	$(BOD_5)_{30}$[b] (mg/L)	Increase in BOD_5:COD ratio[c]
D_{ozone} = 26.1 mg/L min, T = 20 °C						
C_{dye} (g/L)						
0.5	469	84.9	81.9	3.85	33.1	47.5
1.0	956	253.3	73.5	4.06	39.8	37.0
1.5	1426	480.6	66.3	4.34	42.2	28.9
3.0	2804	1354.3	51.7	5.25	47.3	18.7
C_{dye} = 1.0 g/L, T = 20 °C						
D_{ozone} (mg/L min)						
16.7	956	263.9	72.4	4.06	34.8	31.1
26.1	956	253.3	73.5	4.06	39.8	37.0
34.8	956	173.0	81.9	4.06	40.9	55.7
43.6	956	159.7	83.3	4.06	41.3	60.9
69.7	956	147.2	84.6	4.06	42.8	68.5
C_{dye} = 1.0 g/L, D_{ozone} = 26.1 mg/L min						
T (°C)						
10	956	271.5	71.6	4.06	37.1	32.2
20	956	253.3	73.5	4.06	39.8	37.0
30	956	234.2	75.5	4.06	41.0	41.2
40	956	209.4	78.1	4.06	41.7	46.9

[a] $(COD)_0$: COD of the sample before ozonation and $(COD)_{30}$: COD of the sample after 30 min ozonation.

[b] $(BOD_5)_0$: 5-day BOD of the sample before ozonation and $(BOD_5)_{30}$: 5-day BOD of the sample after ozonation.

[c] Increase in BOD_5:COD ratio = $((BOD_5)_{30}/(COD)_{30})$:$((BOD_5)_0/(COD)_0)$.

equation [24]:

$$E = \frac{k_L a}{k_L^o a} \tag{5}$$

values of $k_L a$ can be obtained.

The variations of $k_L a$ with initial dye concentration, applied ozone dose and temperature are plotted in Fig. 3. It is observed that $k_L a$ increases linearly with C_{dye}, D_{ozone} and T, respectively. The best fit of the data in Fig. 3 yields the following model:

$$k_L a = -0.170 + 2.491 \times 10^{-2} C_{dye} + 5.310 \times 10^{-3} D_{ozone} + 5.866 \times 10^{-3} T \tag{6}$$

where the units of C_{dye}, D_{ozone} and T are g/L, mg/L min and °C, respectively. Results of statistical analysis indicate that $k_L a$ has a strong correlation with the three parameters ($R^2 = 0.9533$).

The reason why $k_L a$ increases with C_{dye} can be drawn from the reaction kinetics and absorption theory [23]. When the initial dye concentration increased, more dissolved ozone was consumed which resulted in a lower C_{ozone} as described earlier in decolorization kinetics. Therefore, the driving force of ozone mass transfer from the gas-phase to the liquid-phase, $C^* - C_{ozone}$, increased, so did the rate of ozone mass transfer.

Fig. 3 also indicates the increase of $k_L a$ with D_{ozone}. With increased ozone input, the rate of decolorization increased as shown in Fig. 1b, the increased rate of reaction reduced C_{ozone} and consequently, enhanced the mass transfer of ozone. This is a typical example of gas absorption enhanced by chemical reaction [25].

As for the increase of $k_L a$ with temperature, two effects of temperature should be noted. When temperature rises, the concentration of the dissolved ozone decreases. However, the reaction proceeds faster at higher temperature. According to the results shown in Fig. 1, the overall effect of the temperature rise in the tested temperature range was to increase the rate of dye ozonation, which in turn enhanced the ozone mass transfer.

3.3. *The effect of ozonation on biodegradability*

The ratio of BOD_5-to-COD is usually used to measure the biodegradability of the wastewater [26]. A larger BOD_5-to-COD ratio indicates a higher biodegradability of the wastewater. In this study, the aqueous reactive dye was ozonated to examine the effect of ozonation on biodegradability of the dye solutions. The ozonation was conducted with the gas flowrate of 0.52 L/min and pressure of 82.73 kPa (12 psi) for 30 min. The length of ozonation was selected following a series of preliminary tests, which revealed that changes in BOD_5 and COD were negligible after 30 min. Results are listed in Table 1 where after ozonation, the increase in biodegradability is obvious. The ratio of BOD_5-to-COD increased 18.7–68.5 times. In the meantime, ozonation removed 51.7–84.6% of COD. Therefore, ozonation of the aqueous reactive dye enhanced the biodegradability and removed COD effectively.

4. Conclusions

The decolorization of aqueous C.I. Reactive Blue 15 was a pseudo-first-order reaction with respect to the dye. The apparent rate constant increased with the applied ozone dose and temperature. However, it decreased with initial dye concentration. A logarithmic relationship was derived between the apparent rate constant and initial dye concentration.

Mass transfer of ozone during the decolorization of aqueous reactive dye in the semi-batch reactor was increased linearly with initial dye concentration, applied ozone dose and temperature, respectively. A model was developed to predict the volumetric mass transfer coefficient in the experimental range.

Ozonation improved the biodegradability of the aqueous reactive dye solution. The increase in biodegradability ranged from 18.7 to 68.5 times. Concurrently, ozonation removed wastewater COD effectively. The COD removal ranged from 51.7 to 84.6%

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