Decolorization of Dyes Using Ozone in a Gas-Induced Reactor

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Treatability of aqueous dye solutions using a new gas-induced ozonator was investigated, as well as feasibility of decolorizing dyes using ozone, the ozone utilization efficiency, and the chemical oxygen demand (COD) under various pH values and initial dye concentrations. Experimental results indicate that all of the dyes used can be decolorized within 15 min. For most of the dyes used, ozone decolorizing was more rapid in acidic media. The ozone utilization efficiency can be raised to 90% or higher with proper agitation speeds. The ozone utilization efficiency and COD removal rate increased with an increase in pH value; however, the COD removal remained nearly constant for various categories of dye regardless of the initial dye concentration. The kinetics of decolorization were also examined.

Introduction

Dye manufacturing, textile dyeing and finishing are very common industries in Taiwan, which generate a large amount of wastewater. The composition of dye industry wastewater discharge containing dyes, mordant, sizing agents and dyeing aids are deep in color and highly polluted. Previously, a single chemical coagulation process, in combination with an activated sludge process or activated carbon, was employed to treat this type of wastewater. However, adsorption by activated carbon is an expensive and complicated process, while bio-refractory is limited owing to the low biodegradability of dyes (Grau, 1991). Recently, the Environment Protection Agency (EPA) has placed strict restrictions on the color of wastewater in Taiwan. Ozone processing is a promising alternative.

Ozone is an extremely strong oxidant. It can undergo self-decomposition in an aqueous solution to form hydroxyl free radicals that have a stronger oxidizing capability (Staehelin and Hoigne, 1985; Sotelo et al., 1987). Hence, ozone has many uses. In some commercialized industrial applications, it has been widely accepted as an effective disinfectant and a chemical oxidant (Gould and Weber, 1976; Beltran et al., 1993; Perkins et al., 1995). Studies have reported on the reaction between ozone and dyes (Saunders et al., 1983; Benitez et al., 1993; Gähr et al., 1994), and indicated that ozone possesses an excellent decolorizing capability. However, industrial applications have been limited by the low utilization efficiency of ozone, as well as its high production cost. The low utilization efficiency of ozone can be improved by increasing the retention time of ozone gas in an aqueous solution. In conventional processes, gas utilization efficiency can be improved by linking reactors in a series or by using a compressor to recirculate the unreacted gas back into the processing liquid. However, both of these methods are complex, and require additional accessory equipment, thus increasing the operational cost. Moreover, to improve the utilization of reactive gases, many contactors have been considered, such as the sparged loop reactor, the surface aerator, and the gas-induced reactor. Saravanan and Joshi (1994) indicated that a gas-induced reactor has all of the advantages of other reactors for gas-liquid reactions. A conventional gas-induced reactor consists mainly of a hollow shaft and impeller (Zlokarnik and Judat, 1967; Joshi and Sharma, 1997), or a standpipe with several different types of impellers (Zundelevich, 1979; Mundale and Joshi, 1995). However, their configurations are complicated and high power consumption is required for agitation. Hsu and Huang (1996, 1997) developed a new gas-induced reactor for the same purpose, in which two in-series

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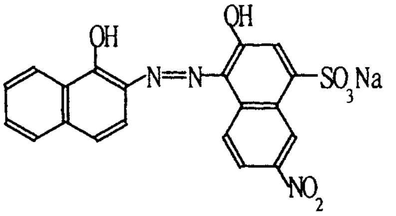
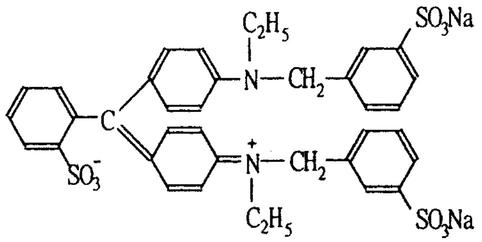
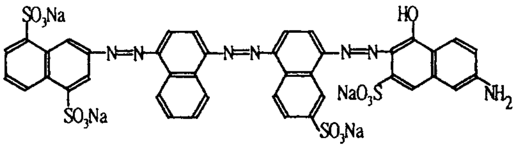
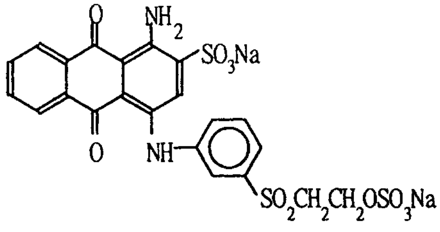
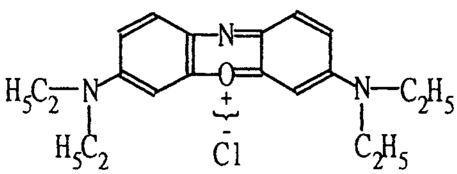
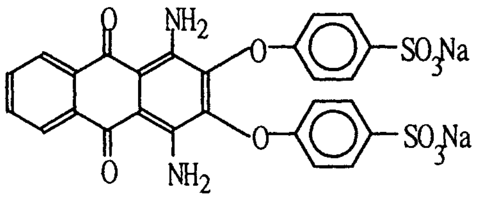
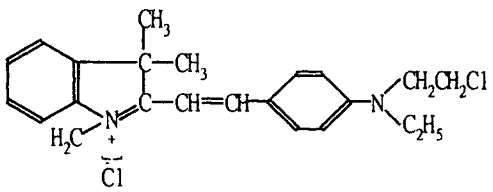
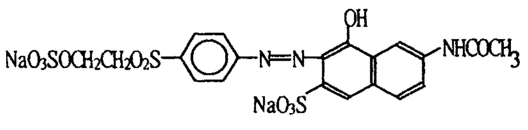
45° pitched-blade turbines were enclosed in a draft tube. Two main characteristics of this device include gas induction and bubble recirculation around the draft tube in the liquid. In our previous work, only a heterogeneous ozone reaction with C.I. Reactive Blue 19 dye at a constant pH value and initial dye concentration was studied. At a stable gas induction, this new reactor demonstrated an ozone utilization efficiency of more than 95%. An improvement in ozone utilization efficiency without any accessory equipment is considered to be a major advantage in cost reduction. In the past, the ozone utilization efficiency on the decomposition of various dyes has rarely been investigated. Notably, each dye has its own molecular structure and differs somewhat in the degree of reaction with ozone. Therefore, this work uses eight different categories of dyes to investigate the performance of this new reactor and its probable application in wastewater treatment of textile dyeing and finishing. The capability of ozone to decolorize and mineralize dyes was also studied. Experimental results show that, for each dye used at various pH values and initial dye concentrations, the ozone utilization efficiency remains higher than 90%. Therefore, the reaction time is effectively shortened.

Table 1. Characteristics of Dyes Used in this Study

C.I. Mordant Black 11	C. I. 42090	C.I. Acid Blue 9	C. I. 14645
λ_{max} = 592 nm 		λ_{max} = 630 nm 	
C.I. Direct Blue 71	**C. I. 34140**	**C.I. Reactive Blue 19**	**C. I. 61200**
λ_{max} = 587 nm 		λ_{max} = 589 nm 	
C.I. Basic Blue 3	**C.I. 51004**	**C.I. Acid Violet 42**	**C.I. 6202**
λ_{max} = 654 nm 		λ_{max} = 548 nm 	
C.I. Basic Red 13	**C.I. 48015**	**C.I. Reactive Orange 16**	**C.I. 17757**
λ_{max} = 524 nm 		λ_{max} = 493 nm 	

Materials and Methods

Materials and procedure

C.I. Mordant Black 11 (MB-11) and C.I. Acid Blue 9 (AB-9) were provided by Chint Chemicals Company (Taiwan). C.I. Reactive Blue 19 (RB-19) and C.I. Reactive Orange 16 (RB-16) were provided by Sumitomo Company (Japan). C.I. Acid Violet 42 (AV-42), C.I. Direct Blue 71 (DB-71), C.I. Basic Blue (BB-3), and C.I. Basic Red 13 (BR-13) were provided by Bayer Company (Germany). The main chemical structures and maximum absorbencies in an aqueous solution were listed in Table 1.

The synthetic wastewater was prepared by dissolving the required amounts (100–500 mg/L ± 10 mg/L) of a single dye in deionized water. The pH values were adjusted to 2.0, 5.0, 7.0, 9.0, or 10.0, respectively, by using 0.1 M NaOH or H_2SO_4 solution (Hewes and Davison, 1971).

The experiment apparatus is shown in Figure 1 (Hsu and Huang, 1996). At the beginning of each run, 7 L of dye solution at the desired concentration and pH was transferred into the reactor. The solution was maintained at 25°C. The flow rate and the concentration of the ozone gas were 210 NL/h and 20 mg/NL, respectively. The concentration of ozone was averaged and used as the feed concentration for ozone gas. The agitation speed was adjusted to 1,800 rpm and the ozone gas was simultaneously introduced into the reactor. In addition the defoamer was added in dribs to eliminate the interference for gas induction in some cases where foaming occurred. The defoamer was a commercial product (KM-73, Shinetsu, Taiwan). Since only a trace amount of defoamer was added, it was expected that it would not interfere with reactions.

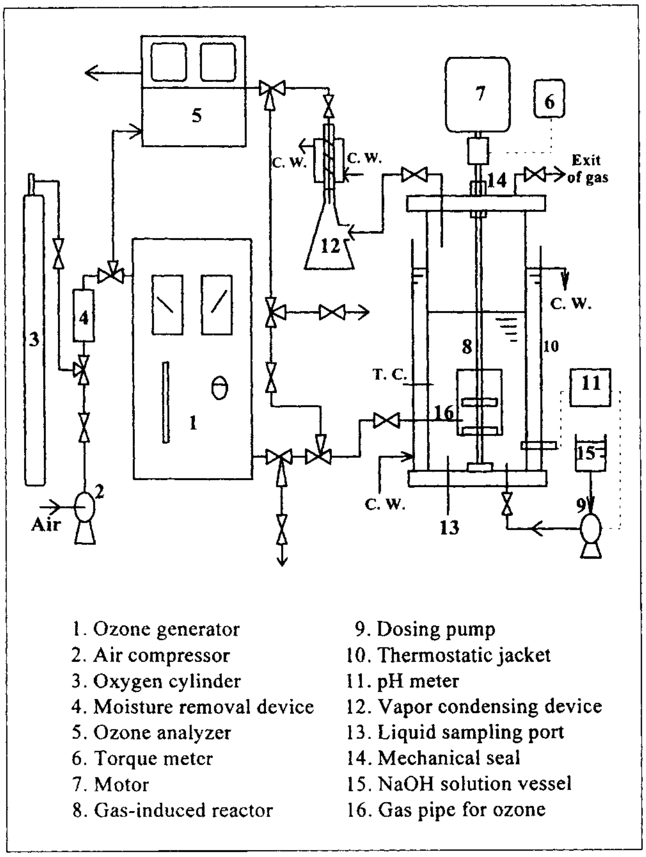


Figure 1. Experimental apparatus.

While the ozone concentration in the effluent gas stream was measured automatically every second by the ozone detector during the reaction, samplings of dye solution were conducted at proper intervals. The color value of each sample was measured employing the American Dye Manufacturers Institute (ADMI) method. The chemical oxygen demand (COD) values were simultaneously determined.

Methods for determination

The ADMI color value of the dye solution was determined employing a UV/Vis Spectrophotometer (Hach DR-4000 colorimeter). During ozonation, the spectrophotometer scans within the visible light range (400–700 nm) and quantified the color of the dye solution.

A Hach COD digester was employed to digest oxidizable organic compounds at 150°C. A UV/Vis Spectrophotometer (Hach DR-4000) was used to determine the COD value of the digested samples at 620 nm (by a built-in digestion method (Jirka and Carter, 1975), U.S. EPA approved).

Equation 1 defines the ozone utilization efficiency, as suggested by Hsu and Huang (1996)

$$U_{O_3} = \frac{W_{O_3,i} - W_{O_3,o}}{W_{O_3,i}} \times 100\% \qquad (1)$$

U_{O_3} values are based on 90% decolorization of the dye solution in which a light color can be observed. $W_{O_3,i}$ and $W_{O_3,o}$ are the total input and output amount of ozone measured in the gas phase.

Results and Discussion

Table 2 summarizes the results of the decolorization of the eight dyes. Among these results, Mordant Black 11 is selected to illustrate the entire scope of these experiments. In species cases, when the BB-3 and BR-13 dye solutions were adjusted to pH 11 and DB-71 was adjusted to pH 2, the appearance of the dye solutions changed, while in the spectrogram, qualitative analysis by absorption became difficult. Consequently, no investigations were conducted under these conditions.

Decolorization time of dyes

(1) Effect of pH Values. Figure 2 shows the decolorization of MB-11 with the same initial dye concentrations at various pH values. This figure also indicates that during ozonation of the ADMI color value of MB-11 disappears gradually. Furthermore, it is evident that the initial decolorization rates within approximately 2 min are almost the same at various pH values. This is because the dye molecules are the primary source of color in the initial stage. Regardless of the pH value, the dye molecules are destroyed easily by ozone and/or hydroxyl free radicals. As the decolorization process continues, after 2 min, intermediate products are generated to such an extent that the difference appears at various pH values. After approximately 4 min, the decolorization rates are much slower

Table 2. Experimental Results for Eight Species of Dyes

C.I. Mordant Black 11					C.I. Direct Blue 71					C.I. Basic Blue 3				
pH	Conc. (mg/L)	$t_{(X=0.9)}$ (s)	U_{O_3} (%)	$(k'_1/k'_2) \times 10^3$ (s^{-1})	pH	Conc. (mg/L)	$t_{(X=0.9)}$ (s)	U_{O_3} (%)	$(k'_1/k'_2) \times 10^3$ (s^{-1})	pH	Conc. (mg/L)	$t_{(X=0.9)}$ (s)	U_{O_3} (%)	$(k'_1/k'_2) \times 10^3$ (s^{-1})
2.0	200±10	396	89.79	9.68/1.55	—	—	—	—	—	2.0	200±10	442	97.16	3.85/6.79
5.0	200±10	426	92.99	—	5.0	200±10	522	89.19	5.06/-	5.0	200±10	479	99.10	3.47/5.51
7.0	200±10	514	93.63	9.12/1.13	7.0	200±10	476	95.25	5.39/-	7.0	200±10	524	99.17	3.28/4.91
10.0	200±10	563	96.64	8.55/1.39	10.0	200±10	427	98.98	5.69/-	9.0	200±10	523	99.07	2.74/5.02
7.0	300±10	772	94.55	5.78/0.85	7.0	300±10	667	95.93	3.84/-	7.0	100±10	269	98.33	6.38/11.29
7.0	400±10	1037	95.06	4.16/0.76	7.0	400±10	931	97.27	2.75/-	7.0	300±10	755	98.99	2.23/3.81
7.0	500±10	1290	95.79	3.25/0.56	7.0	500±10	1045	98.50	2.54/-	7.0	400±10	998	99.19	1.74/3.08
C.I. Acid Blue 9					C.I. Reactive Blue 19					C.I. Acid Violet 42				
pH	Conc. (mg/L)	$t_{(X=0.9)}$ (s)	U_{O_3} (%)	$(k'_1/k'_2) \times 10^3$ (s^{-1})	pH	Conc. (mg/L)	$t_{(X=0.9)}$ (s)	U_{O_3} (%)	$(k'_1/k'_2) \times 10^3$ (s^{-1})	pH	Conc. (mg/L)	$t_{(X=0.9)}$ (s)	U_{O_3} (%)	$(k'_1/k'_2) \times 10^3$ (s^{-1})
2.0	200±10	417	93.63	5.07/-	2.0	200±10	383	86.73	10.63/1.78	2.0	300±10	182	95.98	13.21/-
5.0	200±10	566	95.63	3.79/-	5.0	200±10	390	92.12	9.73/1.59	5.0	300±10	192	99.59	11.46/-
7.0	200±10	602	94.65	3.63/-	7.0	200±10	487	94.51	9.43/1.39	7.0	300±10	206	99.25	10.96/-
10.0	200±10	631	96.47	3.44/-	10.0	200±10	483	97.52	9.37/1.11	10.0	300±10	216	99.66	11.02/-
7.0	300±10	892	96.24	2.48/-	7.0	300±10	740	94.52	6.24/0.83	7.0	200±10	143	99.25	16.01/-
7.0	400±10	1114	97.43	1.94/-	7.0	400±10	990	94.46	4.40/0.67	7.0	400±10	263	99.14	8.32/-
7.0	500±10	1337	98.25	1.61/-	7.0	500±10	1142	94.34	3.69/0.57	7.0	500±10	349	99.50	6.76/-
C.I. Basic Red 13					C.I. Reactive Orange 16									
pH	Conc. (mg/L)	$t_{(X=0.9)}$ (s)	U_{O_3} (%)	$(k'_1/k'_2) \times 10^3$ (s^{-1})	pH	Conc. (mg/L)	$t_{(X=0.9)}$ (s)	U_{O_3} (%)	$(k'_1/k'_2) \times 10^3$ (s^{-1})					
2.0	200±10	270	97.20	6.25/10.35	2.0	200±10	516	83.50	3.85/-					
5.0	200±10	285	97.20	5.76/10.88	5.0	200±10	545	88.92	4.06/-					
7.0	200±10	283	97.72	5.97/10.88	7.0	200±10	470	95.86	4.65/-					
9.0	200±10	296	98.34	6.27/9.22	10.0	200±10	365	99.72	6.40/-					
7.0	300±10	438	98.23	3.88/6.22	10.0	300±10	561	99.85	4.08/-					
7.0	400±10	581	99.45	2.70/4.89	10.0	400±10	778	99.89	2.93/-					
7.0	500±10	722	99.38	2.52/3.92	10.0	500±10	932	99.99	2.51/-					

Note: X = fractional conversion; $Q_g = 210$ NL/h; $C_{O_3,i} = 20.0 \pm 0.1$ mg/NL.

than the initial rate for any pH value. This is because most dye molecules are destroyed and the persistent intermediate products become the primary substances. Figure 2 also indicates that a decrease in the pH value increases the dye decolorization rate. Evidently, the resonance effect within the chromophore of the dye structure greatly enhances the electron density, which in turn is affected by the ozone molecule electrophilic attack (Sotelo et al., 1989). At low pH values, a greater extent of decolorization is favored by a more direct ozone attack, since decolorization is associated with the destruction of chromophore. The increase in pH value may accelerate ozone decomposition, forming more hydroxyl free radicals (·OH) (Hoigne and Bader, 1976, 1983; Gurol and Singer, 1982). This causes a decrease in available ozone molecules and a less selective ozone attack on chromophore. Consequently, a longer reaction time for decolorization is required. Similar results were also obtained for BB-3, BR-13, AV-42, AB-9, and RB-19. Figure 3 presents the decolorization behavior of RO-16. Unlike MB-11, the decolorization curves of RO-16 at various pH values are smooth, with the decolorization rate increasing as the pH increases. This reaction of RO-16 is likely due to both the resonance effects of the RO-16 dye molecules and the electrophilic attack by hydroxyl free radicals. In alkaline media (such as pH = 10) the naphthalenic ring of RO-16 exhibits higher electron densities. Resonance from the dissociated hydroxyl group (that is, $—\ddot{\underset{..}{O}}^-$) and the $—\ddot{N}HCOCH_3$ group, which donates electrons acting as electron releasing groups, enhances the electron density in the ring and renders the electron-rich naphthalenic ring to be more susceptible to attack by ·OH radicals.

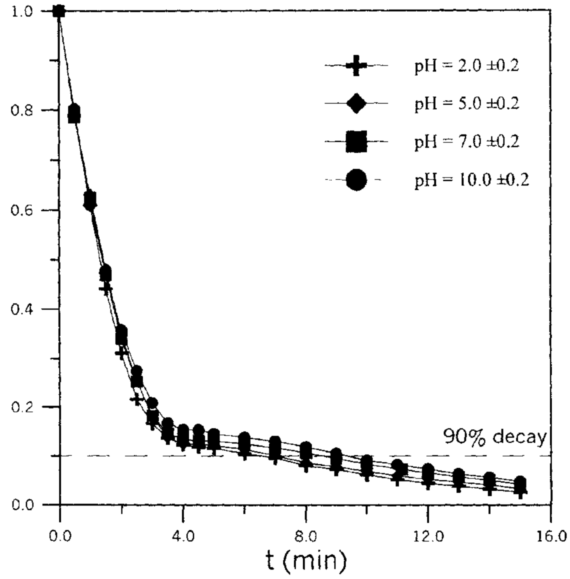


Figure 2. Normalized decolorization of MB-11 at different pH values with same initial concentration of dyes.

$T = 298$ K, $N = 1{,}800$ rpm, $Q_g = 210$ NL/h, $C_{O_3,i} = 20.0 \pm 0.1$ mg/NL, $C_{do} = 200 \pm 10$ mg/L.

(2) Effect of Initial Dye Concentration. Figure 4 shows the relationship between (ADMI/ADMI$_o$) and time. It is evident

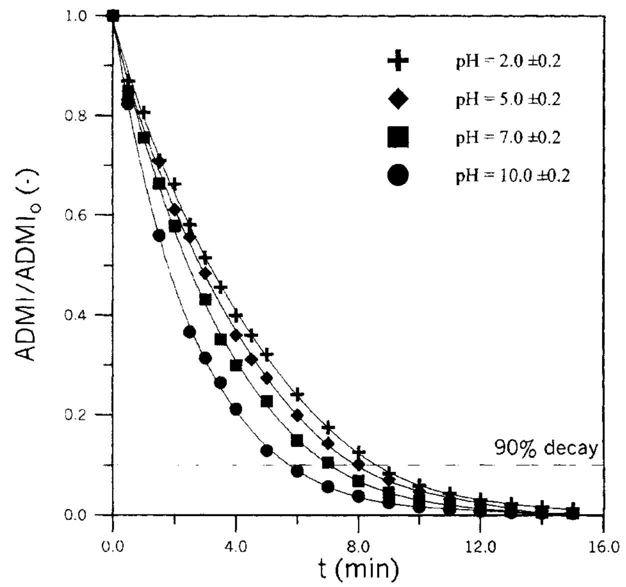


Figure 3. Normalized decolorization of RO-16 at different pH values.

T = 298 K, N = 1,800 rpm, Q_g = 210 NL/h, $C_{O_3,i}$ = 20.0 ± 0.1 mg/NL, C_{do} = 200 ± 10 mg/L.

that the decolorization time required is dependent upon different initial concentration of MB-11. Results also indicate that, at the concentration of C_{do} = 200 ± 10 mg/L ($ADMI_o$ = 3425 value), 90% decolorization could be reached within 10 min, whereas approximately 22 min are required for higher concentrations such as C_{do} = 500 ± 10 mg/L ($ADMI_o$ = 8,500 value). Furthermore, the decolorization times required at higher dye concentrations are greater than those at lower dye concentrations. This is due to the constant input ozone concentration, which is maintained in this study; therefore, more time is required at higher dye concentrations. All required decolorization times were extremely short. Consequently, the decolorization by ozone is remarkable and feasible for the treatment of different dye concentrations in manufacturing wastewater of textile dyeing and finishing plants. Similar results are obtained for all other dyes used.

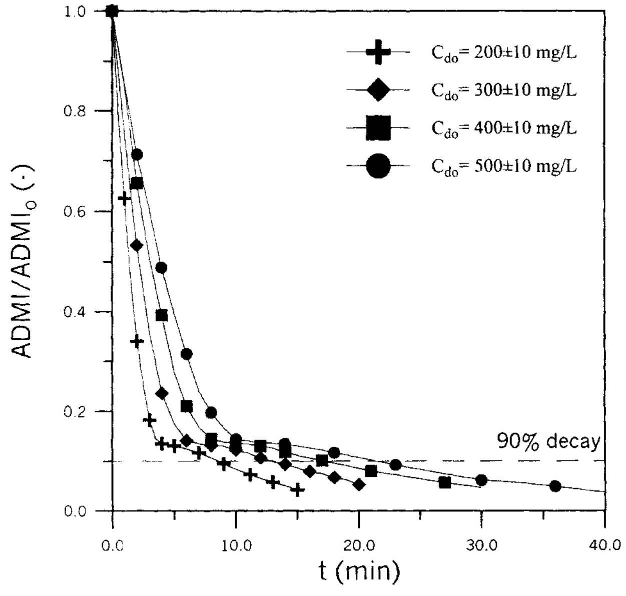


Figure 4. Normalized decolorization of MB-11 at different initial concentrations of dye with the same pH values.

T = 298 K, N = 1,800 rpm, Q_g = 210 NL/h, $C_{O_3,i}$ = 20.0 ± 0.1 mg/NL, pH = 7.0 ± 0.2.

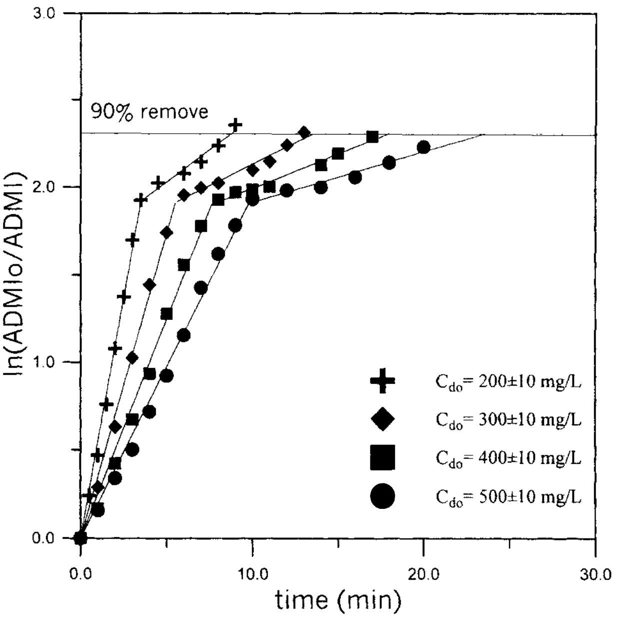


Figure 5. Variation of ln(ADMIo/ADMI) of MB-11 with time at different initial dye concentration during ozone processing.

T = 298 K, N = 1,800 rpm, Q_g = 210 NL/h, $C_{O_3,i}$ = 20.0 ± 0.1 mg/NL, pH = 7.0 ± 0.2.

Kinetics analysis for decolorization

Saunders et al. (1983) found that the reaction between the dye and ozone is an instantaneous reaction and, in the liquid film, ozone is consumed completely in a semi-batch process. Therefore, they proposed that the kinetics model of dye with ozone was a pseudo first-order reaction. In this work, the decolorization of the eight dyes is also performed by semi-batch process. The pseudo first-order expression is assumed to describe the heterogeneous ozonation of experimental dyes with an associated instantaneous chemical reaction. Furthermore, the input ozone concentration is constant and no residual ozone remains in the bulk liquid as 90% ADMI color value is removed. In addition, ozone utilization efficiency is very high in this study (Table 2). Hence, it is possible to consider that there is an almost constant ozone influence, which can be incorporated into the overall reaction rate constant k'. However, some of the dyes have two different overall rate constants (Figure 5) and the respective k'_1 and k'_2 are calculated by

$$\ln \frac{\mathrm{ADMI}_{(\mathrm{section\ 1})}}{\mathrm{ADMI}_{0,1}} = k'_1 t \qquad (2)$$

for the first section, while

$$\ln \frac{\text{ADMI}_{(\text{section}\,2)}}{\text{ADMI}_{0,2}} = k_2' t \qquad (3)$$

for the second section. $\text{ADMI}_{0,1}$ represents the initial ADMI color value at $t = 0$, and the $\text{ADMI}_{0,2}$ represents the ADMI color value at the standing point of the second section. According to Figure 5, the variation of $\ln(\text{ADMI}_0/\text{ADMI})$ of MB-11 with time at different initial concentrations are separated into two sections before 90% decolorization. It can be considered that ozone molecules and/or hydroxyl free radicals mainly attack the dye molecules in the first section, and attack the intermediate products in the second section. The decolorization rate in the first section is faster than that in the second section, which is because the MB-11 molecules are destroyed and form the yellow persistent decomposition intermediate products (Perkins et al., 1995). Similar results were found in RB-19 (figure not shown here). In contrast, the decolorization rates in the second section for DB-71 and AB-9 are faster than those in the first section. This may be attributed to ADMI color value of the intermediate products that are more easily decreased by ozonation. Figure 6 shows the $\ln(\text{ADMI}_0/\text{ADMI})$ vs. time plot for RO-16 (others are not shown here). Due to the slight influence of intermediate products, RO-16 and other dyes (namely, DB-71, AB-9, and AV-42) are depicted by one straight line to represent the decolorization kinetics before 90% decolorization. Table 2 summarizes the overall decolorization rate constants and ozone utilization efficiency for each dye.

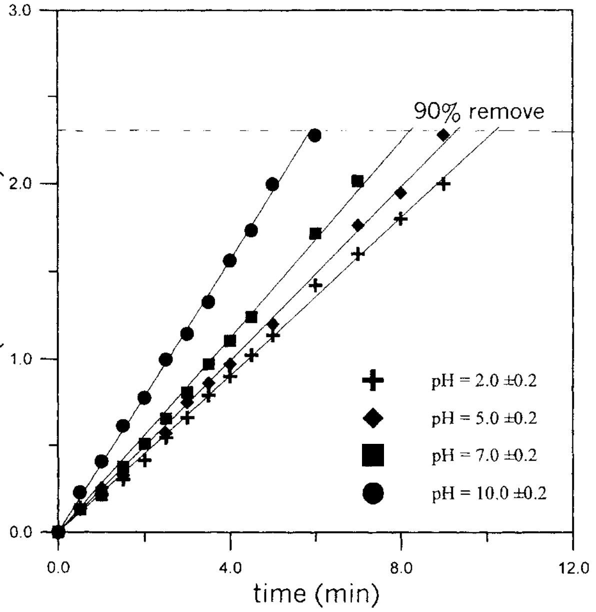


Figure 6. Variation of ln(ADMIo/ADMI) values of RO-16 with time at different pH values during ozone processing.

$T = 298$ K, $N = 1{,}800$ rpm, $Q_g = 210$ NL/h, $C_{O_3,i} = 20.0 \pm 0.1$ mg/NL, $C_{d0} = 200 \pm 10$ mg/L.

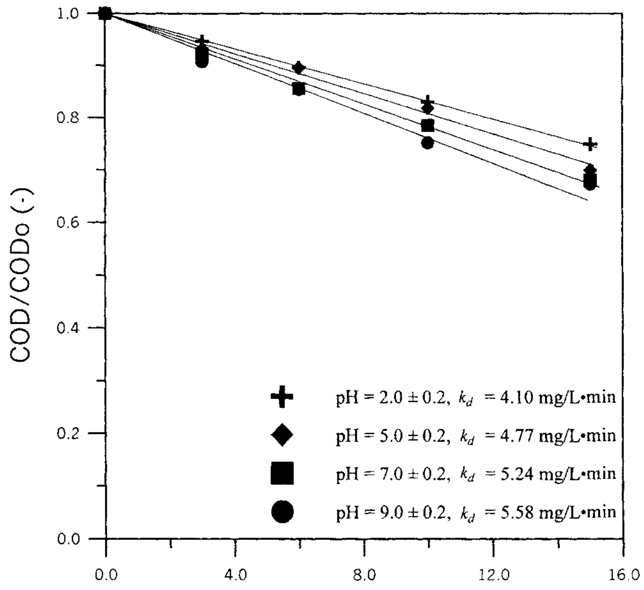


Figure 7. Effect of pH value on normalized COD removal for MB-11 during ozone processing.

$T = 298$ K, $N = 1{,}800$ rpm, $Qg = 210$ NL/h, $C_{O_3,i} = 20.0 \pm 0.1$ mg/NL, $C_{d0} = 200 \pm 10$ mg/L.

COD elimination

(1) Effect of pH Value. Figure 7 shows the variation of normalized COD removal of MB-11 with time at various pH values. The normalized COD removal increases with an increase in the pH value. It is considered that at higher pH values, higher fractions of ozone are decomposed to form ˙OH radicals (Hoigne and Bader, 1976, 1983; Gurol and Singer, 1982). Since ˙OH radicals have a stronger oxidation potential than ozone molecules, the ˙OH radicals attack dye molecules and intermediates more vigorously than would be expected for a molecular ozone. As a result, the higher the pH values, the faster the mineralization will be. Singer and Gurol (1983) also obtained similar results as they treated phenol using ozone in a semibatch reactor.

(2) Effect of Initial Concentration of Dyes. Figure 8 shows the COD removal of MB-11 plotted against ozonation time to compare with literature. It is evident that during ozonation at a constant pH value, the COD removal rate appears to remain almost constant ($k_d = 5.22 \pm 0.02$ mg/L·min). Tzitzi et al. (1994) reported similar results. However, in Tzitzi et al. the COD removal rate is about 1.5 mg/L·min, which is much smaller than 5.22 ± 0.02 mg/L·min, as proved herein. The removal consistency of a given amount of COD is independent of the initial dye concentration. The COD/O_3 ratio is summarized in Table 3.

Ozone utilization efficiency

Figure 9a shows the ozone utilization efficiency for the decolorization of MB-11 at various pH values with the same initial dye concentration. Ozone utilization efficiencies are more than 90% and increase with increasing pH value. At

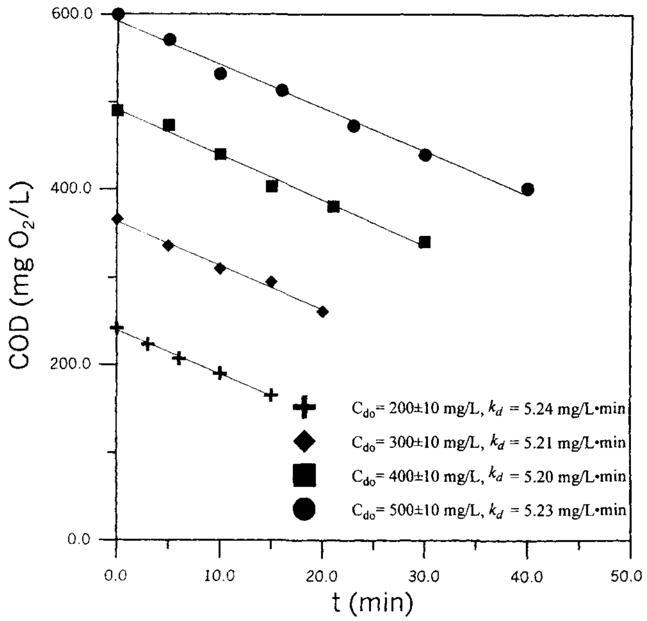


Figure 8. Effect of initial concentration of dyes on COD removal for MB-11 during ozone processing.

$T = 298$ K, $N = 1{,}800$ rpm, $Q_g = 210$ NL/h, $C_{O_3,i} = 20.0 \pm 0.1$ mg/NL, pH = 7.0 ± 0.2.

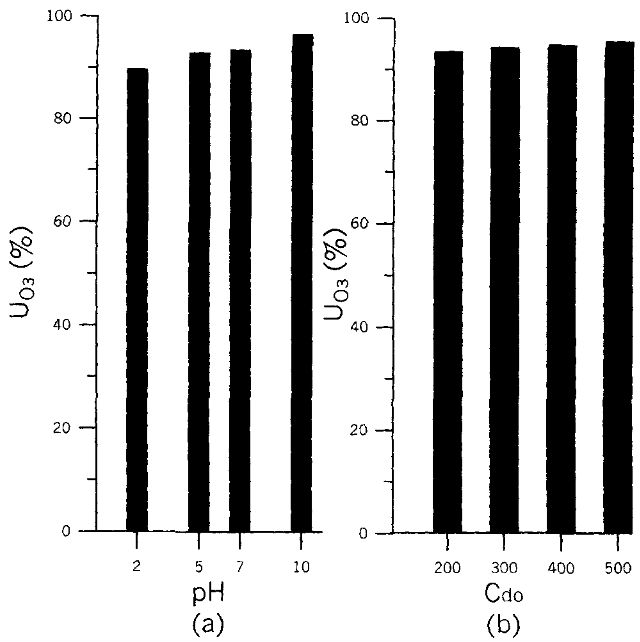


Figure 9. Effect of initial concentration and pH of MB-11 dye on ozone utilization efficiency during ozone processing.

$T = 298$ K, $N = 1{,}800$ rpm, $Q_g = 210$ NL/h, $C_{O_3,i} = 20.0 \pm 0.1$ mg/NL, (a) $C_{do} = 200 \pm 10$ mg/L; (b) pH = 7.0 ± 0.2.

higher pH values, more ˙OH free radicals with higher oxidation-reduction potential tend to be produced from ozone self-decomposition (Hoigne and Bader, 1976, 1983; Gurol and Vatistas, 1987). For that reason, more ozone molecules can dissolve into the aqueous solution and a higher OUE can be obtained. As showing in Figure 9b, at different initial dye concentrations with the same pH value, OUE still remains high (> 95%) and is almost independent of the initial dye concentration. Table 2 illustrates the overall results. With the exception of RO-16, DB-71, and RB-19 dye in acidic medium, an OUE of greater than 90% can be obtained. This unique characteristic is beneficial to the treatment of industrial wastewater containing various dyes.

Conclusions

This work has demonstrated that the ozone utilization efficiency increased with an increase in pH value. When a newly developed gas-induced reactor was employed, ozone utiliza-

Table 3. COD/O_3 Ratios of Eight Species of Dyes

C.I. Acid Blue 9			C.I. Acid Violet 42			C.I. Direct Blue 71		
pH	Conc. (mg/L)	COD/O_3	pH	Conc. (mg/L)	COD/O_3	pH	Conc. (mg/L)	COD/O_3
2.0	200 ± 10	0.527	2.0	300 ± 10	0.535	—	—	—
5.0	200 ± 10	0.515	5.0	300 ± 10	0.696	5.0	200 ± 10	0.462
7.0	200 ± 10	0.518	7.0	300 ± 10	0.835	7.0	200 ± 10	0.545
10.0	200 ± 10	0.641	10.0	300 ± 10	0.989	10.0	200 ± 10	0.569
7.0	300 ± 10	0.685	7.0	200 ± 10	0.678	7.0	300 ± 10	0.546
7.0	400 ± 10	0.652	7.0	400 ± 10	0.502	7.0	400 ± 10	0.626
7.0	500 ± 10	0.480	7.0	500 ± 10	0.525	7.0	500 ± 10	0.739
C.I. Mordant Black 11			C.I. Reactive Blue 19			C.I. Direct Blue 71		
pH	Conc. (mg/L)	COD/O_3	pH	Conc. (mg/L)	COD/O_3	pH	Conc. (mg/L)	COD/O_3
2.0	200 ± 10	0.460	2.0	200 ± 10	0.387	2.0	200 ± 10	0.535
5.0	200 ± 10	0.508	5.0	200 ± 10	0.464	5.0	200 ± 10	0.531
7.0	200 ± 10	0.567	7.0	200 ± 10	0.565	7.0	200 ± 10	0.623
10.0	200 ± 10	0.592	10.0	200 ± 10	0.599	10.0	200 ± 10	0.685
7.0	300 ± 10	0.538	7.0	300 ± 10	0.560	10.0	300 ± 10	0.690
7.0	400 ± 10	0.537	7.0	400 ± 10	0.565	10.0	400 ± 10	0.620
7.0	500 ± 10	0.555	7.0	500 ± 10	0.656	10.0	500 ± 10	0.601

tion efficiency obtained can be more than 90% regardless of pH values and initial dye concentrations. Hence, ozone treatment of various dye solutions can be very rapid and efficient. Generally, only 15 to 22 min is required for a 90% dye solution decolorization at a concentration of 500 ± 10 mg/L. The overall decolorization rate constant depends on the various dyes and ozone utilization efficiency. In particular, MB-11, RB-19, BB-3, and BR-13 have two overall decolorization rate constants and the others used have only one. The COD elimination rates are found to be nearly constant regardless of the initial dye concentration; however, it increases with increasing pH value.

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Notation

AMDI = color value of dye solution during ozone processing
$ADMI_0$ = initial color value of dye solution
$ADMI_{0,1}$ = initial ADMI color value at $t = 0$
$ADMI_{0,2}$ = ADMI color value at the standing point of section 2
C_{do} = initial dye concentration, mg/L
$C_{O_3,i}$ = ozone input concentration at 273 K, 101.3 kPa, mg/NL
k_d = COD elimination rate constant, mg/L·min
k' = overall decolorization rate constant, s^{-1}
k'_1 = overall decolorization rate constant of the first section, s^{-1}
k'_2 = overall decolorization rate constant of the second section, s^{-1}
N = impeller speed, rpm
Q_g = ozone input flow rate at 273 K, 101.3 kPa, NL/h
t = reaction time, s
T = temperature, K
U_{O_3} = ozone utilization efficiency, %
$W_{O_3,i}$ = total weight of ozone fed to the reactor, mg
$W_{O_3,o}$ = total weight of ozone leaving the reactor, mg
X = fractions of conversion
λ_{max} = maximum absorption wavelength of dye in aqueous solution, nm

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