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Ozonalytic kinetic order of dye decoloration in aqueous solution

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Abstract

The intrinsic kinetic order of reaction between a dye (Acid Blue 9) and dissolved ozone in aqueous phase was measured by a pulse-ejection microreactor (PEMR) in this research. The reaction orders and reaction rate constants were evaluated by the variation of initial slope method, the half-life method, and the general order equation. Results of this study indicated that the commonly literature-cited pseudo-first-order may not be suitable for all ozonation conditions. The pseudo-first-order was only valid with an ozone to dye molar ratio (Z) between 5.57 and 9.31. When the value of Z increased from 13.91 to 30.83, the reaction order increased rapidly from 1.03 to 1.76. On the other hand, when the value of Z was smaller than 1.74, the reaction order seemed closer to zero order. Furthermore, the reaction order may not be constant throughout the treatment process. It might vary with variation of ozone to dye ratio as the reaction is proceeding.

Keywords: Ozonation; Liquid–liquid reaction; Acid Blue 9; Kinetics; Textile dyeing

1. Introduction

Textile wastewater is strongly colored and creates an environmental and aesthetic problem. Wastewater from textile industry is an important pollution source in Taiwan. Effluents from textile industry contain high concentrations of inorganic and organic chemicals and are characterized by residual COD and strong color. Resistance of dyes to biological degradation has made color removal from textile wastewaters more difficult, as they are not readily degraded under the aerobic conditions prevailing in biological treatment plants. In Taiwan, to comply with environmental regulations, wastewater that is produced from dye manufacturers and dyeing industries has to adhere to COD < 100 mg/L and ADMI color index < 550 unit standards. Due to the difficulty of removing color from wastewater, the 1998 ADMI standard (400 units) was modified to the present standard. Even with the present standard, many manufacturers still have difficulty in complying with this regulation. Currently, there are no economically attractive technologies to achieve color removal from dyeing wastewater [1]. Ozonation is one of the attractive alternatives for solving the problem of color in dyehouse effluent [2–4]. In addition, Wang et al. [5] stated that the ozonation processes enhanced the biodegradability of biorefractory compounds.

The reaction mechanisms of ozonalytic 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 be simultaneously existing during the reaction processes [5]. At basic pH, ozone rapidly decomposes to yield hydroxyl and other radical species in solution. Under acidic conditions, ozone can directly react with organic substrates as an electrophile. Ozone is very effective for

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decolorizing dye wastewaters, because it attacks conjugated double bonds and these are often associated with color.

The pseudo-first-order equation was the most cited for ozone decolorization systems [1,4,6]. Wu and Wang [6] studied the ozonation of reactive black 5 in a semi-batch reactor (gas–liquid system). The decolorization of dyes is of first order with respect to ozone and the dye, respectively. When the amount of ozone was in excess, the reaction was pseudo-first-order with respect to dye. They reported that the decolorization of the azo dye by ozone was a pseudo-first-order reaction with respect to dye and the apparent rate constant declines logarithmically with increased initial dye concentration. The decolorization rate constant can be determined from the slope of the semi-logarithmic plot of color versus treatment time indicated as follows [1].

$$\ln(C_t/C_0) = K_d \times t \tag{1}$$

where C_t and C_0 are dye concentrations at reaction times $t = t$ and $t = 0$, respectively. K_d stands for the pseudo-first-order reaction rate constant (L/min).

However, the experiments mentioned above were conducted in a gas–liquid system, not liquid–liquid system. In a gas–liquid system, where ozone was absorbed into water and simultaneously underwent reaction, the rate-limiting step in the ozonation of dye containing wastewater was the mass transfer of ozone from the gas phase to the wastewater [6,7]. There was no reliable and generally valid model for the qualitative prediction of the mass transfer coefficient of ozone [6]. In gas–liquid reactors, the rate of reaction in the liquid phase depends on both the reaction rate constant and the coefficient of mass transfer from gas to liquid. Under the kinetic regime of absorption with reaction, an accurate measurement of the rate constant is possible. On the other hand, in the diffusion controlled regime as in the case of ozonation of dye, the rate constant cannot be measured easily because the system behavior would depend on the mass transfer coefficient [8,9]. As a consequence, the commonly used pseudo-first-order reaction model may not be suited to describe the intrinsic kinetics of liquid–liquid conditions. The relationship between the apparent rate constant and the initial dye concentration was not studied in detail in literature [6]. The kinetics of aqueous ozonation processes plays an important role in assessing the efficiency and feasibility of treating dye contaminated wastewater. Furthermore, it could provide a tool for evaluating the health effects of ozone exposure to humans, crops and forests [10]. Therefore, there is a need to study the intrinsic liquid reaction kinetics of ozonalytic reactions to further understand the kinetic reaction of ozonation and its possible effect on the overall kinetic reaction of the gas–liquid ozonation process.

2. Materials and methods

2.1. Pulse-ejection microreactor (PEMR)

The study was performed in a 70 mL pulse-ejection microreactor (PEMR) depicted in Fig. 1. This microreactor consisted of a main body of reactor column and three horizontal baffles which were located within the reactor column to assure a perfect mixing (PM). An injector was installed vertically at the upper center of the reactor. The whole reactor was clamped on a base stand, which in turn was fixed to a steel stand by supporters. Four suction safety bulbs were hung over the top of the reactor, with four suction lines interconnected for sampling. Through sampling ports 1–3, samples withdrawn from different regimes of PEMR were analyzed for testing the degree of mixing and the kinetic analysis.

2.2. Gas-induced reactor (GIR)

The GIR was used as an ozone-dissolving apparatus for this research. The novel GIR (Fig. 2) was first developed by Hsu et al. [11–14]. By installing an additional short draft tube surrounding the impeller, a strong vortex can be created which accelerates the solubilization of ozone and benefits the recycling and reclaiming of the escaping ozone. When the desired ozone concentration was reached, then 50 mL of ozone solution was discharged directly through a submerged interconnecting pipeline to the PEMR without exposure to the atmosphere to avoid the escape of any ozone.

2.3. Ozonation

Saturated ozone solution was prepared by GIR. Fifty milliliters of the saturated ozone solution was directly transferred to the PEMR through a submerged interconnecting under-liquid pipe. Twenty milliliters of dye solution was measured by a syringe located at the upper center of the PEMR. The syringe was previously stoppered with silicone rubber before dye solution ejected into the PEMR. The safety suction bulbs had been previously adjusted and calibrated for a given amount of 5 mL samplings at 0.5 s intervals.

Ozone was produced by a laboratory ozone generator system (model RXO-5) which when supplied with air produces a maximum of 20 mg O_3/L. The concentration of ozone during experimentation was 5 mg/L air.

The ozone concentration was measured through the determination of the concentration of iodine which was produced from the reaction of ozone with neutral potassium iodide. The concentration of iodine was determined spectrophotometrically at a wavelength of 400 nm [15,16]. The interference of the measurements had been reported to be negligible [17,18]. Analytical grade chemicals were used throughout the experiments.

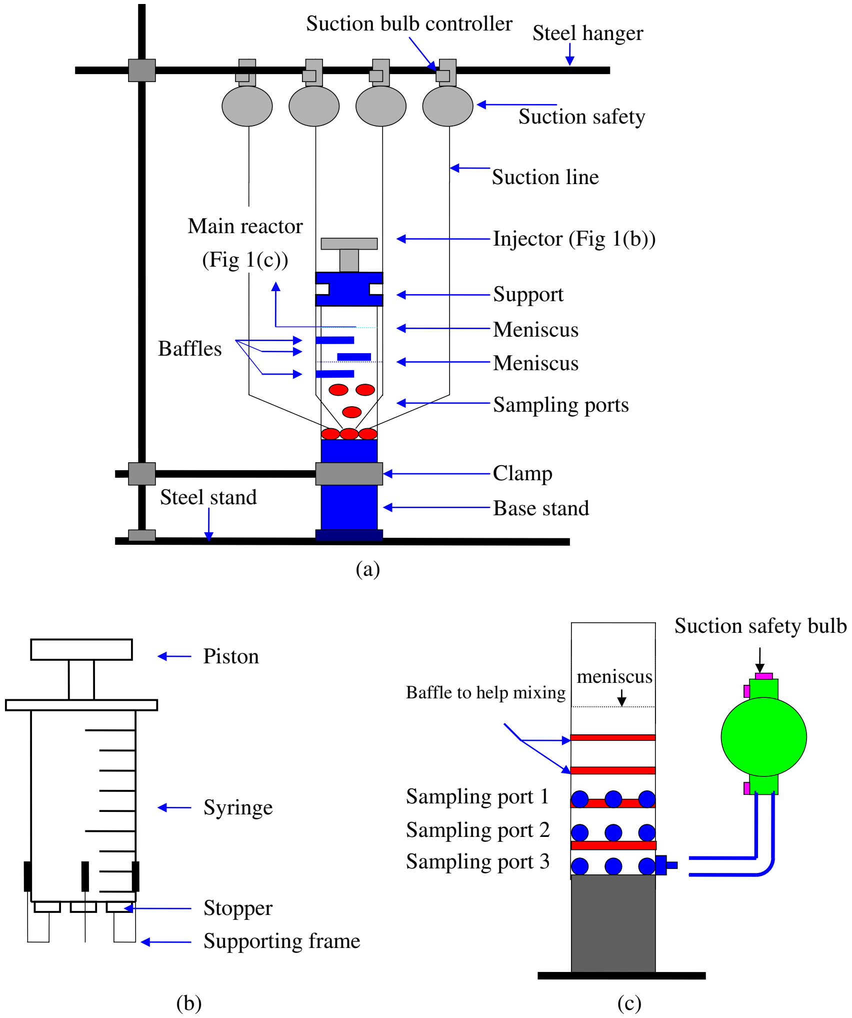

Fig. 1. The experimental set-up of the pulse-ejection microreactor (PEMR): (a) experimental set-up, (b) injector made of a 50 mL syringe, (c) main reactor of PEMR showing sampling ports at different regimes.

One milliliter of 0.01 N iodine is equivalent to 240 μg of ozone.

Acid Blue 9 ($C_{37}H_{34}N_2Na_2O_9S_3$, C.I. 42090, FW 792.84) concentration was measured spectrophotometrically at its characteristic wavelength (λ_{max}, 630 nm). Acid Blue 9 was purchased from Acros Organics, USA. The chemical structure of Acid Blue 9 is represented in Fig. 3.

3. Results and discussion

3.1. Perfect mixing

The mixing time is one of the most critical factors for investigation of the intrinsic kinetics of fast reactions such as ozonation in aqueous solution, which determines the deviation from the "true kinetics". To ensure a perfect mixing in the PEMR, six runs of mixing test were performed in this test. When mixing 20 mL (10 mg/L) of dye with 50 mL of distilled water, it only took less than 0.5 s to reach the well-mixing status at the top, middle and bottom locations of the PEMR. The final mixing concentration of Acid Blue 9 measured at 630 nm was about 2.74 mg/L which was reached within 0.5 s at all three sampling locations as indicated in Table 1.

3.2. Kinetic analysis

Twelve different initial concentrations of Acid Blue 9 were tested in the PEMR. The initial dye concentration ranges were from 1.29 to 285.71 mg/L. Samples were taken and analyzed at 0, 0.5, 1.0, 1.5 and 2.0 s. The fractional conversions (*f*) of these tests are shown in Table 2. Experimental results indicated that the low concentration ranges of dyes had higher fraction of conversions.

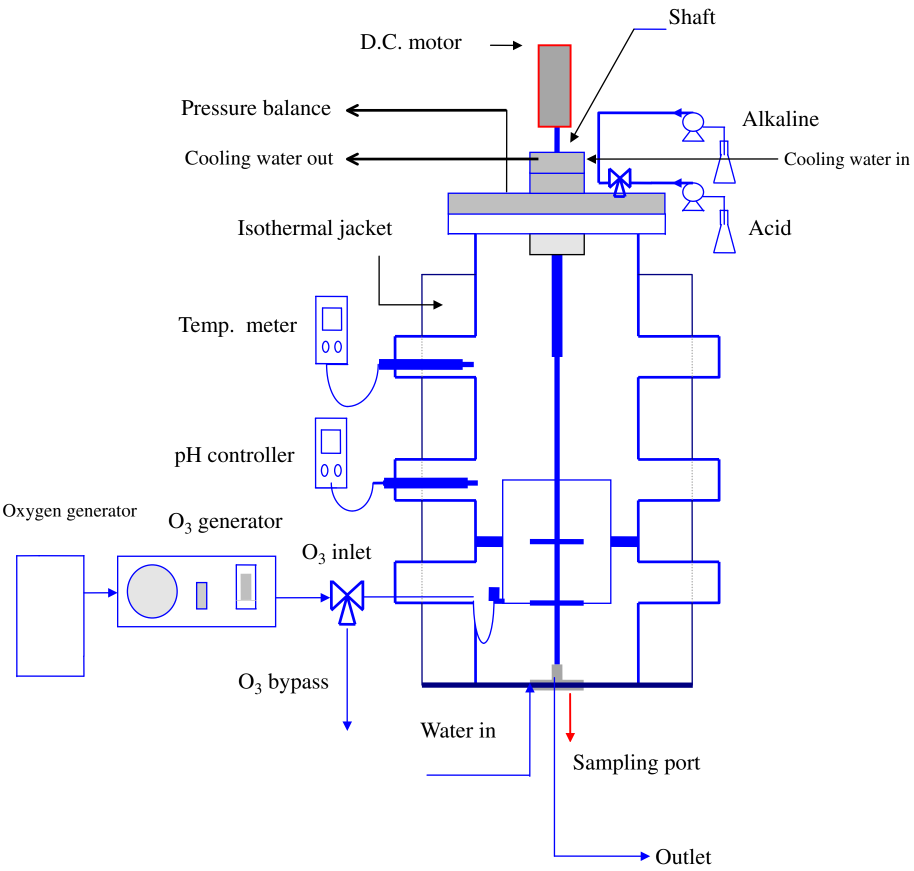

Fig. 2. Schematic diagram of experimental ozone dissolution system, GIR (gas-induced reactor).

To further investigate the fast aqueous ozonation kinetics, three different kinetic analysis methods were used in this research [19].

(1) Variation of initial slope
The kinetic order (n) is

$$n=\frac{\log\left(\frac{dC_1}{dt}\right)-\left(\frac{dC_2}{dt}\right)}{\log C_1-\log C_2} \tag{2}$$

where C_1 and C_2 are different initial concentrations of paired experiments, and dC_1/dt and dC_2/dt are differential initial reaction rates deduced by measurement of the initial slope of the concentration–time curve.

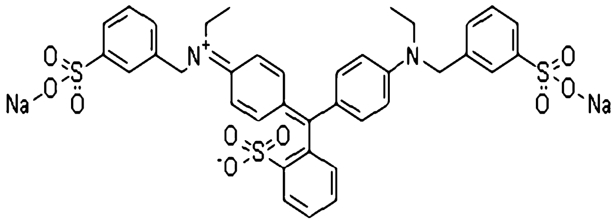

Fig. 3. Chemical structure of Acid Blue 9.

(2) Half-life method
The method consists of determining the time taken for the initial concentration of a reactant to be reduced by a factor of two. Experiments are carried out at two or more different initial concentrations (C_1, C_2). If the half-life (τ_1, τ_2) is independent of initial concentrations, then the reaction is of first order. If the half-life varies with initial concentration, the results τ_1 and τ_2 may have the expression:

$$\frac{\tau_1}{\tau_2}=\left(\frac{C_2}{C_1}\right)^{n-1} \tag{3}$$

where

$$n=1+\frac{\log\frac{\tau_1}{\tau_2}}{\log\frac{C_2}{C_1}} \tag{4}$$

Table 1
Tests for a perfect mixing (sampling time 0.5 s, 29 °C, pH 7.2 ± 0.1)

Sampling location	Dye concentration (mg/L)						
	Run no.						Mean[a]
	1	2	3	4	5	6	
Top	2.73	2.71	2.64	2.67	2.65	2.84	2.73 ± 0.07
Middle	2.72	2.84	2.81	2.64	2.67	2.74	2.74 ± 0.08
Bottom	2.72	2.84	2.81	2.64	2.67	2.74	2.74 ± 0.08

[a] Data expressed in $\overline{X} \pm \sigma$ ($n = 6$).

(3) General order equation

Considering the following general forward equation

$$\frac{1}{C_t^{n-1}} - \frac{1}{C_0^{n-1}} = (n-1)k_n t \tag{5}$$

and assuming that t_f is the time at which the initial concentration (C_0) has fallen to C_f (i.e. the residual concentration with fractional conversion f), we have:

$$\frac{1}{C_f^{n-1}} - \frac{1}{C_0^{n-1}} = (n-1)kt_f \tag{6}$$

At two different fractional conversions f_1 and f_2, we have

$$\frac{1}{C_{f_1}^{n-1}} - \frac{1}{C_0^{n-1}} = (n-1)kt_{f_1} \tag{7}$$

and

$$\frac{1}{C_{f_2}^{n-1}} - \frac{1}{C_0^{n-1}} = (n-1)kt_{f_2}, \tag{8}$$

respectively.

Division of Eqs. (7) and (8) gives:

$$\frac{t_{f_1}}{t_{f_2}} = \frac{\dfrac{1}{C_{f_1}^{n-1}} - \dfrac{1}{C_0^{n-1}}}{\dfrac{1}{C_{f_2}^{n-1}} - \dfrac{1}{C_0^{n-1}}} = \frac{\left(\dfrac{C_0}{C_{f_1}}\right)^{n-1} - 1}{\left(\dfrac{C_0}{C_{f_2}}\right)^{n-1} - 1} \tag{9}$$

Substituting experimental data C_0, C_{f_1}, C_{f_2}, t_{f_1} and t_{f_2} into Eq. (9), the order n can be obtained.

The estimated kinetic reaction orders calculated from these methods were in good agreement with each other as indicated in Table 3. The results revealed that the kinetic order for ozone degradation of Acid Blue 9 was concentration-dependent; the Z values played a role of controlling factor; and different ozone to dye molar ratios (Z) yielded different kinetic orders. Simulation results of the general order model are shown in Fig. 4. As the Z values were less than 0.17, there was no observation of significant dye degradation. Very low orders of kinetics were found as the values of Z remained within 1.39–1.74 with the kinetic reaction order found to be less than 0.01. At this range, the reaction rate constants ranged from 6.40×10^{-7} to 9.60×10^{-6} (mg/L/s). Whereas the Z ratio was within a range of 5.57–9.31, the reaction order was close to pseudo-first-order as commonly cited in literature [1,4,6,20–22]. For example, Saunders et al. [23] studied the ozonation of decoloration of methylene blue with 90% decoloration and reported pseudo-first-order kinetics with a stoichiometric ratio (Z) around or a little less than 10. The reaction rate constants were increased from 0.67 to 7.07 (s^{-1}). When the Z ratios were greater than 9.31, the kinetic orders increased from 1.08 to 1.76. The reaction rate constants increased sharply from 7.07×10^5 to 8.82×10^5 ($(\mathrm{mg/L})^{1-n}\,\mathrm{s}^{-1}$). The larger the Z values, the faster the reactions observed were. The

Table 2
Fractional conversion (f) of Acid Blue 9 at various initial dye concentrations (C_0) ($f = 1 - (C_t/C_0)$, pH 7.2 ± 0.1, 29 °C, ozone concentration 3.37 mg/L)

C_0[a]	Reaction time									
	0 s		0.5 s		1 s		1.5 s		2 s	
	Mean	SD[b]	Mean	SD[b]	Mean	SD[b]	Mean	SD[b]	Mean	SD[b]
1.29	0.00	0.000	0.97	0.005	0.98	0.004	0.98	0.004	0.99	0.013
1.43	0.00	0.000	0.97	0.001	0.98	0.005	0.98	0.005	0.99	0.011
2.14	0.00	0.000	0.87	0.011	0.90	0.011	0.90	0.011	0.96	0.012
2.29	0.00	0.000	0.86	0.011	0.89	0.012	0.89	0.012	0.93	0.014
2.86	0.00	0.000	0.76	0.022	0.87	0.001	0.87	0.001	0.91	0.011
4.29	0.00	0.000	0.72	0.021	0.78	0.020	0.78	0.020	0.88	0.021
5.71	0.00	0.000	0.34	0.082	0.60	0.080	0.60	0.080	0.69	0.010
7.14	0.00	0.000	0.31	0.080	0.59	0.011	0.59	0.011	0.70	0.003
22.86	0.00	0.000	0.01	0.012	0.12	0.031	0.12	0.031	0.21	0.004
28.57	0.00	0.000	0.01	0.020	0.05	0.002	0.05	0.002	0.10	0.003
228.57	0.00	0.000	0.00	0.000	0.00	0.000	0.00	0.000	0.00	0.000
285.71	0.00	0.000	0.00	0.000	0.00	0.000	0.00	0.000	0.00	0.001

[a] C_0 = initial dye concentration (mg/L).
[b] SD = standard deviation.

Table 3
Kinetic order analysis of dye degradation by ozone (initial ozone concentration 3.37 mg/L, 29 °C, pH 7.2 ± 0.1)

Z^a	The general order method		The half-life method		The variation of initial slope method	
	Reaction order $n_{(g)}$	Rate constant[b] $k_{(g)}$	Reaction order $n_{(h)}$	Rate constant[b] $k_{(h)}$	Reaction order $n_{(i)}$	Rate constant[b] $k_{(i)}$
0.14	0.00 ± 0.000	–	0.00 ± 0.000	–	0.00 ± 0.000	–
0.17	0.00 ± 0.000	–	0.00 ± 0.000	–	0.00 ± 0.000	–
1.39	0.01 ± 0.000	6.40×10^{-7}	0.01 ± 0.000	6.40×10^{-7}	0.01 ± 0.000	6.40×10^{-7}
1.74	0.01 ± 0.000	9.60×10^{-6}	0.01 ± 0.000	9.60×10^{-6}	0.01 ± 0.000	9.60×10^{-6}
5.57	1.00 ± 0.002	0.76	1.00 ± 0.004	0.76	1.00 ± 0.001	0.76
6.96	1.00 ± 0.002	0.76	1.00 ± 0.003	0.76	1.00 ± 0.002	0.76
9.31	1.08 ± 0.003	7.07	1.07 ± 0.003	7.15	1.08 ± 0.006	7.07
13.91	1.10 ± 0.001	10.74	1.09 ± 0.001	9.85	1.10 ± 0.005	10.74
17.36	1.25 ± 0.003	123.16	1.25 ± 0.005	123.65	1.24 ± 0.007	123.16
18.58	1.25 ± 0.005	131.29	1.24 ± 0.002	123.29	1.25 ± 0.004	131.29
27.81	1.76 ± 0.002	8.15×10^5	1.77 ± 0.001	9.25×10^5	1.76 ± 0.003	8.15×10^5
30.83	1.76 ± 0.001	8.82×10^5	1.78 ± 0.003	10.88×10^5	1.76 ± 0.002	8.82×10^5

[a] Z = ozone to dye stoichiometric ratio.
[b] Unit = $(\mathrm{mg/L})^{1-n}\,\mathrm{s}^{-1}$.

reaction rate constant decreased with increasing initial dye concentrations. These results were in agreement with Konsowa [24]; the author reported that the reaction rate of dye (Isma Fast Red 8B) oxidation was found to increase with increasing ozone concentration in the gas phase (air–ozone) and decrease with increasing dye concentration.

When Z is greater than 5.57, the relationship between Z and kinetic order (n) can be described in a linear equation as follows (Fig. 5):

$$n = 0.0327Z + 0.7422 \tag{10}$$

where the correlation coefficient (R^2) was about 0.9385.

When considering a gas–liquid system, Carpentier [22] had pointed out that an enhancement factor (E) had to be incorporated into the gas to liquid mass transfer (i.e. gas absorption) term when a chemical reaction was simultaneously participating in the gas–liquid reaction system such as the ozone$_{(g)}$ to liquid reaction:

$$N_A = k_L a C_A \times E \tag{11}$$

in which, N_A expresses the gas absorption rate ($\mathrm{mol\,s^{-1}\,m^{-2}}$), $k_L a$ is the liquid side volumetric mass transfer coefficient ($\mathrm{s^{-1}}$), while E is called the enhancement factor which is defined as the ratio of the rate of ozone absorption in the presence of a chemical reaction to the maximum rate of physical absorption [22].

Considering a continuous semi-batch ozone inflowing system, the dye concentration is originally high enough to retain a pseudo-first-order reaction (i.e. Z = 5.57–10.00), and the stoichiometric ratio Z may increase rapidly as the decoloration proceeds. The reaction order may increase to over 1.7 as indicated in Eq. (10) at the final stage of reaction. Thus, a faster reaction is occurring when the reaction is approaching the final

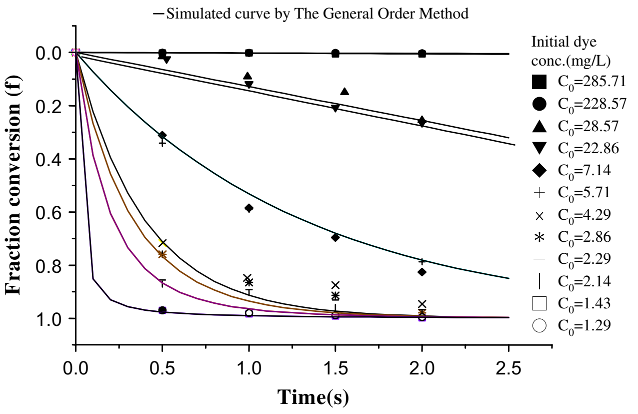

Fig. 4. Fractional conversion ($f = 1 - (C_t/C_0)$) of Acid Blue 9. Initial conditions were 3.37 mg O_3/L, pH 7.2 ± 0.1, and 29 °C.

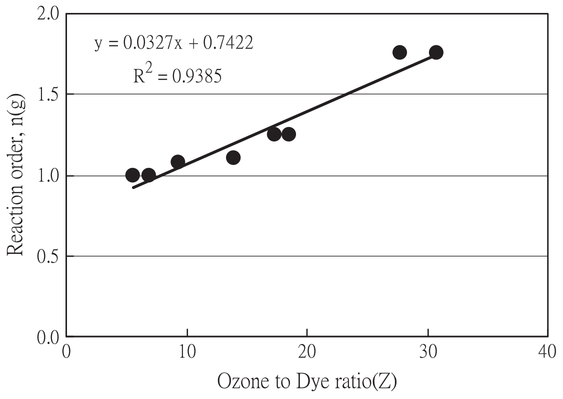

Fig. 5. The relationship between ozone to dye molar ratio (Z) and reaction order ($n_{(g)}$).

stage. Therefore, the enhancement factor might be varying and correspondingly increasing, which implies that a varying mass transfer rate is occurring simultaneously and may result in more complicated kinetic patterns. In other words, in a single ozonation system, the enhancement factor might be varying depending upon the sequential variation of the stoichiometric factor Z during the reaction. The varying kinetic order in the liquid–liquid reaction can affect the overall kinetic order which involves the gas to liquid mass transfer phenomena.

Results also imply that in a gas–liquid ozonation, the enhancement factor E may vary from a low value at the initial stage of ozonation to a higher value at the final stage; the greater the Z value as the reaction proceeds, the faster the reaction and hence the greater the enhancement factor obtained near the final stage of ozonation. Thus, the overall gas–liquid reaction kinetics will be also varying during the whole course of ozonation.

4. Conclusion

Liquid–liquid ozonation of Acid Blue 9 in batch tests revealed varying kinetic order ranging from 0 to 1.76. The kinetic order variation depends on the stoichiometric ratio of ozone to dye (Z). Near zero order can be applied to values of Z below 1.74. At values of Z from 5.57 to 9.31, the pseudo-first-kinetic order was observed. When Z was greater than 13.91, kinetic orders of 1.10–1.76 were found. A linear equation could be used to describe the relationship between Z and n when Z was greater than 5.57. The results also implied that the enhancement factor might change significantly during the process of a given reaction which might consequently affect gas–liquid reaction kinetics.

References

[1] Alaton IA, Balcioglu IA, Bahnemann DW. Advanced oxidation of a reactive dyebath effluent: comparison of O_3, H_2O_2/UV-C and TiO_2/UV-A processes. Water Res 2002;36(5):1143–54.

[2] Sarasa J, Roche MP, Ormad MP, Gimedo E, Puig A, Ovelleiro JL. Treatment of a wastewater resulting from dyes manufacturing with ozone and chemical coagulation. Water Res 1998;32(9):2721–7.

[3] Koch M, Yediler A, Lienert D, Insel G, Kettrup A. Ozonation of hydrolyzed azo dye reactive yellow 84. Chemosphere 2002;46:109–13.

[4] Ince NH, Tezcanli G. Reactive dyestuff degradation by combined sonolysis and ozonation. Dyes Pigments 2001;49:145–53.

[5] Wang C, Yediler A, Lienert D, Wang Z, Kettrup A. Ozonation of an azo dye C.I. Remazol Black 5 and toxicological assessment of oxidation products. Chemosphere 2003;52:1225–32.

[6] Wu J, Wang T. Ozonation of aqueous azo dye in a semi-batch reactor. Water Res 2001;35(4):1093–9.

[7] Shu HY, Huang CR. Degradation of commercial azo dyes in water using ozonation and Uv enhanced ozonation process. Chemosphere 1995;31(8):3813–25.

[8] Andreozzi R, Caprio V, Insola A, Tufano V. Measuring ozonation rate constants in gas–liquid reactions under the kinetic–diffusional transition regime. Chem Eng Comm 1996;143:195–204.

[9] Andreozzi R, Caprio V, D'Amore MG, Insola A, Tufano V. The ozonation of 2-hydroxypyridine in aqueous solutions. Ind Eng Chem Res 1991;30:2098–104.

[10] Yao CC, Haag WR. Rate constant for direct reactions of ozone with several drinking water contaminants. Water Res 1991;5(7):761–73.

[11] Hsu YC, Chang HC. Onset of gas self-induction and power consumption after gas induction in an agitated tank. J Chem Technol Biotechnol 1995;64:137–48.

[12] Hsu YC, Huang KF. Effects of geometrical factors on liquid mixing in a gas-induced agitated tank. J Chem Technol Biotechnol 1997;68(2):222.

[13] Hsu YC, Peng RY, Hung CJ. Onset of gas induction, power consumption, gas holdup and mass transfer in a new gas-induced reactor. Chem Eng Sci 1997;52(21/22):3883–91.

[14] Hsu YC, Hung CJ. Characteristics of a new gas-induced reactor. AICHE J 1996;42(11):3146–52.

[15] Peng RY, Wu CJ. The quality control during the instant noodle processing-II. A spectrophotometric method for determination of the peroxide value in fried frying oil. Acad Rep Natl Taipei Inst Technol 1973;6:1–4.

[16] Shechter H. Spectrophotometric method for determination for ozone in aqueous solutions. Water Res 1973;7:729–39.

[17] Tyrrell RM. Lethal cellular changes induced by near-ultraviolet radiation. Acta Biol. Med Germ 1979;38:1259–69.

[18] Sutherland JC, Griffin KP. Absorption spectrum of DNA for wavelengths greater than 300 nm. Radiat Res 1981;86:399–410.

[19] Cooper AR, Jefferys GV. Chemical kinetics and reactor design. Edinburgh, England: Oliver and Boyd; 1971.

[20] Hoigne J, Bader H, Haag WR, Staehelin J. Rate constant reactions of ozone with organic and inorganic compounds in water—III. Water Res 1985;19:993–1004.

[21] Hoigne J, Bader H. Rate constant reactions of ozone with organic and inorganic compounds in water—I. Water Res 1983;17:173–83.

[22] Carpentier JC. Gas–liquid adsorptions and reactions. In: Drew TB, et al, editor. Advances in chemical engineering. New York: Academic Press; 1981.

[23] Saunders FM, Gould JP, Southerland CR. The effect of solute competition on ozonolysis of industrial dyes. Water Res 1983;17(10):1407–19.

[24] Konsowa AH. Decolorization of wastewater containing direct dye by ozonation in a batch bubble column reactor. Desalination 2003;158:233–40.