

NOTES

Reactor Dynamics in the Evaluation of Photocatalytic Oxidation Kinetics

INTRODUCTION

The process of photocatalytic oxidation has received considerable attention recently as a treatment of water contaminated with organic pollutants. UV-illuminated titanium dioxide initiates the production of electrons and holes, resulting in the oxidation of organic compounds to carbon dioxide and simple inorganic acids. Numerous researchers have shown that the initial rate kinetics of organic removal are described well by the Langmuir–Hinshelwood (LH) expression (1–4)

$$-\frac{dC}{dt} = \frac{K_1 C}{1 + K_2 C} \quad (1)$$

where C represents the aqueous organic concentration and K_1 and K_2 are constants. In these investigations it has been assumed that true photocatalytic reaction rates are proportional to dC/dt , determined from measurements of organic concentration. Where completely illuminated batch reactors have been used, this is indeed the case. Correspondingly, the constants K_1 and K_2 are found to be functions of several physicochemical conditions.

Several other kinetic studies on photocatalytic oxidation have used a plug flow-type reactor where the suspension is exposed to the appropriate light source for only a fraction of the time. A completely mixed reservoir is present where the solution is collected and sampling is performed (Fig. 1, top).

The objective of this note is to provide rigorous analysis of the reactor configuration shown in Fig. 1 (top) and to demonstrate

that the apparent reaction rate measured in the reservoir, dC/dt , is not equal to the actual photocatalytic oxidation rate, but rather is a composite expression consisting of elements originating in chemical kinetics and reactor dynamics.

DERIVATION OF REACTION RATE

The system given in Figure 1 (bottom) consists of a continuously stirred tank reactor (CSTR, the reservoir), maintained under unlighted conditions to prevent any reaction, and a plug-flow reactor (PFR) where the photocatalytic reactions take place. The appropriate mass balance around the CSTR yields

$$-\frac{dC_2}{dt} V_1 = Q(C_2 - C_1) \quad (2)$$

where C_2 represents the organic concentration throughout the CSTR and C_1 is the concentration entering the reservoir after treatment through the lighted PFR. The symbols Q and V_1 represent the flow rate through the photoreactor and the volume of the CSTR, respectively.

At high conversion through the PFR, the observed rate is not limited by the reaction kinetics, but by exposure to the light. Thus C_1 approaches zero and Eq. (2) reduces to

$$-\frac{dC_2}{dt} = \frac{Q}{V_1} C_2 = \frac{C_2}{\theta_1} \quad (3)$$

Therefore, for conditions of low flow or low substrate concentration, the rate is controlled only by θ_1 , the space time in the CSTR.

The photoreactor is considered a simple

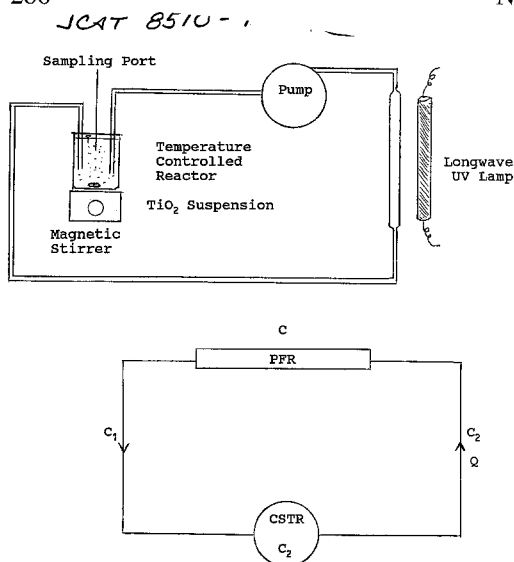


FIG. 1. Diagram showing flow-through photoreactor with a completely mixed reservoir. Top: sample actual system; bottom: schematic diagram.

PFR with the general design equation given as (5)

$$\int_{C_2}^{C_1} \frac{dC}{r} = - \int_0^{V_2} \frac{dV}{Q} \quad (4)$$

where V_2 is the total volume of the PFR and r is the true photocatalytic oxidation reaction rate expressed on a unit volume basis.

Experiments using batch (as well as flow-through) reactors have suggested that photocatalytic oxidation kinetics for organic pollutants follow LH kinetics (1, 2):

$$r = \frac{K_1 C}{1 + K_2 C} \quad (5)$$

Substitution of this expression into the general PFR equation (4) and subsequent integration [assuming that Eq. (5) is valid for all concentrations over a small conversion in the PFR] yield

$$\ln \frac{C_2}{C_1} + K_2 (C_2 - C_1) = K_1 \theta_2 \quad (6)$$

where θ_2 is the space time of the PFR, V_2/Q . This expression, coupled with Eq. (2),

via C_2 and C_1 , describes the measured organic removal rate, dC_2/dt . There is no closed form for solving Eq. (2) and only numerical solutions are possible. Therefore, constants determined from plots exemplifying Eq. (5), i.e., $1/r$ versus $1/C$, do not represent the actual reaction kinetics.

Two simplified cases for Eq. (5) can be examined. For example, at low C , Eq. (5) reduces to a first-order reaction rate:

$$r = K_1 C \quad (7a)$$

$$\ln C_2/C_1 = K_1 \theta_2. \quad (7b)$$

Therefore,

$$- \frac{dC_2}{dt} = \frac{1}{\theta_1} [1 - \exp(-K_1 \theta_2)] C_2 = K_{app} C_2 \quad (7c)$$

In this case the CSTR/PFR rate expression [Eq. (7c)] does follow a reaction order (first order) identical to that of the true reaction [Eq. (7a)]. However, the apparent constant, K_{app} , is not equal to the actual rate constant (K_1); rather it is also a function of reactor volumes and flow rate. Nevertheless, for low values of $K_1 \theta_2$, i.e., small conversions per pass through the PFR, the term $1 - \exp(-K_1 \theta_2)$ approaches $K_1 \theta_2$. Correspondingly, under these conditions,

$$K_{app} = \frac{\theta_2}{\theta_1} K_1 = \frac{V_2}{V_1} K_1. \quad (8)$$

Similarly, at high C , Eq. (5) becomes zero order,

$$r = K_1/K_2 \quad (9a)$$

$$C_2 - C_1 = \theta_2 K_1/K_2, \quad (9b)$$

and

$$- \frac{dC_2}{dt} = \frac{V_2 K_1}{V_1 K_2} = K_{app}. \quad (9c)$$

Again, the apparent reaction order follows that of the actual reaction (zero order) and reactor volumes must be considered when analyzing rate constants.

TABLE 1

Parameters Used in the Calculation of Initial Photocatalytic Oxidation Rates

Parameter	Ref. (3)	Ref. (4)	
Substrate	4-Chlorophenol	Benzene	
θ_2 (min)	0.3	0.125	
Q (ml/min)	250	2400	
V_1 (ml)	175	300	
V_2 (ml)	75	300	
Values calculated in this study using Eqs. (2) and (6)			
K_1 (min ⁻¹)	0.048	0.281	
K_2 (mol/liter) ⁻¹	1.75×10^4	1.31×10^4	
$K_1\theta_2$	1.44×10^{-2}	3.51×10^{-2}	
Values from direct fit of Eq. (5)			
		Apparent ^a	Doubled ^b
K_1 (min ⁻¹)	0.020	0.272	0.702
K_2 (mol/liter) ⁻¹	1.74×10^4	1.26×10^4	1.8×10^4
K_1V_1/V_2 (min ⁻¹)	0.047	0.272	0.702

^a Rates used are for apparent rates; authors doubled rates to compensate for dark reaction time.

^b Values presented by authors.

DISCUSSION

Since the order with respect to organic concentration does not change when considering the CSTR/PFR system in the extremes of both zero- and first-order reactions, LH kinetics should also be nearly identical. However, along this transition, the rate changes from being proportional to $1 - \exp(-K_1\theta_2)$ to K_1 , thus invalidating any information to be extracted from continuous apparent rate versus concentration curves. Even though the term $1 - \exp(-K_1\theta_2)$ is equal to $K_1\theta_2$ under certain conditions, not considering the V_2/V_1 term can result in large errors in calculating values for K_1 and K_2 .

Using data from previous work (Table 1) (3, 4), values of K_1 and K_2 were calculated by fitting Eqs. (6) and (2), using a Newton-Raphson iteration and a nonlinear, least-squares program, to the initial oxidation rates. The values of K_1 and K_2 are presented in Table 1. These data and the calculated curves, corresponding to LH kinetics in a CSTR/PFR system, are presented in Fig. 2. The apparent initial rates from Ref.

(4) were doubled by the authors to compensate for the split of residence time between the lighted and dark reactors. The unmodified rates are used in the present analysis.

Nonetheless, a nonlinear, least-squares fit of Eq. (5) to these data also generates an excellent description of the data. The calculated lines in this case are essentially identical to those found using the ideal curves [Eqs. (2) and (6)]. The constants, K_1 and K_2 ,

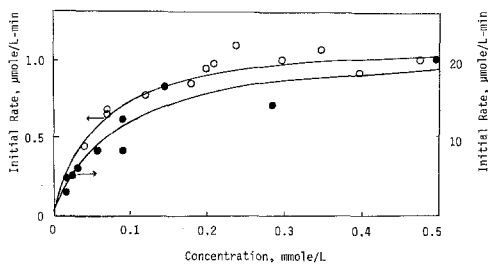


FIG. 2. Initial photocatalytic oxidation rate as a function of organic concentration. The data points are from Ref. (3), \circ , 4-chlorophenol, and Ref. (4), \bullet , benzene. The curves result identically from nonlinear, least-squares fits of Eqs. (2) and (6) as well as Eq. (5) to the data. The resulting constants are presented in Table 1.

determined using Eq. (5) are also listed in Table 1 which indicate that the K_2 values are practically the same for the two evaluation processes; the values of K_1 are different for the first data set, but nearly the same for the second. From Eq. (8), it is seen that the apparent K_1 must be normalized by V_1/V_2 to define the actual K_1 value. Table 1 shows that $K_1 V_1/V_2$ from Eq. (5) is essentially identical to K_1 from the CSTR/PFR model. Consequently, K_1 values reported by other investigators differ by a factor of V_2/V_1 from the true value.

Using the adjusted K_1 values, Eqs. (9a) and (9c) suggest that the K_2 values from both evaluations should be equal, as noted in Table 1. One reason that the values determined by both methods are essentially equal is that the criterion that $K_1\theta_2$ be small is met. Only in the case of a plug-flow photoreactor with no dark reservoir or the fortuitous case of $V_1 = V_2$ (with $K_1\theta_2$ small) would the values be identical. It is also seen from Table 1 that doubling the rate did not produce the true values for K_1 and K_2 (although some of the discrepancy likely results from the statistical analyses used).

Therefore, initial photocatalytic oxidation rate constants that are determined by data fit to the LH rate equation using CSTR/PFR systems (3, 4, 6, 7) must be viewed cautiously. Analogously, attempts to model experimental data using LH expressions (4) may not be valid, although the mathematical relationships are similar. Thus for the LH expression in certain circumstances, rate constants for the flow-through reactor and the actual kinetics are directly proportional and generalizations, such as linear comparisons with hydroxyl radical rate constants (8), are valid. The difference becomes very important in trying to compare actual values of rate or adsorption constants or in investi-

gating multicomponent organic mixtures as performed by Al-Ekabi *et al.* (3).

As a concluding note, photochemical reactions are dependent upon lighted surface area, not a reactant concentration. Therefore, the lighted area and solution depth become important in rate calculations. Using identical reactor configuration and conditions, these phenomena are constant and do not affect rate comparisons. Nevertheless, with so many investigators working on photocatalytic oxidation due to its great promise as a water treatment process, a large amount of published kinetic data is not useful to other researchers if the entire reaction system is not completely defined.

REFERENCES

1. Okamoto, K.-I., Yamamoto, Y., Tanaka, H., and Itaya, A., *Bull. Chem. Soc. Jpn.* **58**, 2023 (1985).
2. Augugliaro, V., Palmisano, L., Sclafani, A., Minero, C., and Pelizzetti, E., *Toxicol. Environ. Chem.* **16**, 89 (1988).
3. Al-Ekabi, H., Serpone, N., Pelizzetti, E., Minero, C., Fox, M. A., and Draper, R. B., *Langmuir* **5**, 250 (1989).
4. Turchi, C. S., and Ollis, D. F., *J. Catal.* **119**, 483 (1989).
5. Levenspiel, O., "Chemical Reaction Engineering," 2nd ed. Wiley, New York, 1972.
6. Matthews, R., *J. Phys. Chem.* **91**, 3328 (1987).
7. Al-Ekabi, H., and Serpone, N., *J. Phys. Chem.* **92**, 5726 (1988).
8. Turchi, C. S., and Ollis, D. F., *J. Catal.* **122**, 178 (1990).

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