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Reply to Comments on "Reactor Dynamics in the Evaluation of Photocatalytic Oxidation Kinetics"

In their comments on our note (*1*), Turchi and Wolfrum agree with our statement that in a CSTR/PFR system, the apparent reaction rate is a composite expression consisting of elements originating in chemical kinetics and reactor dynamics. This was the principal point of our note. Since the study of photocatalytic oxidation kinetics is now ubiquitous, evaluation of true chemical kinetic constants is of utmost importance.

Our analysis of the PFR in the two-reactor system is only valid under steady-state conditions. For example, in a field application of photocatalytic oxidation, a continuous flow/withdrawal to the CSTR may be employed under steady-state conditions. In a batch recirculation system, however, Eq. (6) of our note is invalid as the discussers correctly point out. (The $K_1\Theta_2^2$ term in Eq. (9) of their analysis should be subtracted; however, this term is neglected anyway.) We express our thanks to Turchi and Wolfrum for their comments and appreciate their derivation to correct our analysis as (equation numbers refer to our original note)

$$K_{\mathrm{app}} = \frac{V_2}{V_1 + V_2} K_1. \tag{8}$$

In the case of a recirculating system without the CSTR mixing reactor ($V_1 = 0$), no modification of the determined constants is necessary.

TABLE 1

Calculation of Initial Photocatalytic Oxidation Rates

Parameter	Data from:		
	Ref. (*3*)		Ref. (*2*)
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), modified)		
K_1 (min^{-1})	0.068		0.554
K_2 (mol/liter)$^{-1}$	1.73×10^4		1.29×10^4
$K_1\Theta_2$	2.04×10^{-2}		6.93×10^{-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
$K_1 (V_1 + V_2)/V_2$ (min^{-1})	0.067	0.554	

[a] Rates used are for apparent rates.

[b] Values presented by authors for doubled rates.

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Consequently, we can modify our analysis using the corrected equation,

$$\ln \frac{C_2(t) - \Theta_2\, dC_2(t)/dt}{C_1(t)} + K_2[C_2(t) - \Theta_2\, dC_2(t)/dt - C_1(t)] = K_1\Theta_2, \quad (6)$$

coupled with the CSTR mass balance (Eq. (2)). These equations have been fitted to the initial oxidation rates using a Newton–Raphson iteration and a nonlinear, least-squares program. The revised results are presented in Table 1 and compared with a direct fit of the Langmuir–Hinshelwood equation (5). Both methods are essentially identical in fitting the data and the K_2 values are approximately the same. The apparent K_1 must be normalized by $(V_1 + V_2)/V_2$ to define the actual K_1 value. Again, discrepancies between our calculated values and those of Ref. (*2*) develop due to the statistical analyses used.

Overall, our basic premise does not change; reactor volumes must be considered when analyzing CSTR/PFR systems. This can be done by adjusting the observed photocatalytic oxidation rate, as did Turchi and Ollis (*2*), or by modifying the calculated rate constants to account for reactor volumes. Although Turchi and Ollis (*2*) have considered reactor dynamics in their kinetic analysis, other investigators have not.

We are encouraged by the fact that the methodology based on the CSTR/PFR system successfully describes the concentration profile in a pilot-scale photocatalytic system, as the discussers point out. A complete understanding of the kinetics of this promising water treatment process will enable its fullest utilization.

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ALLEN P. DAVIS
OLIVER J. HAO

Department of Civil Engineering
University of Maryland
College Park, Maryland 20742

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