

DEGRADATION OF GASEOUS TRICHLOROETHYLENE OVER THIN-FILM TiO₂ PHOTOCATALYST

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ABSTRACT

Photocatalytic degradation (PCD) of gaseous trichloroethylene (TCE) over thin-film TiO₂ was examined in a continuous flow system regarding mixing condition of baffle, inlet concentration of TCE, and face velocity of gas flow. The effect of mixing with baffle on the PCD rate of TCE was found to be positive with conditions of simultaneous low inlet concentration and high face velocity. It was found that the effect of mixing could be improved by installation of baffle, based on the tanks-in-series and dispersion models using RTD data in the existence of baffle. The baffles acted as CSTR behavior in the reactor. The PCD rate continuously increased linearly with TCE inlet concentration regardless of the tendency of Langmuir-Hinshelwood (L-H) kinetics. The face velocity increased the PCD rate too. In the long run, it could be concluded that the PCD rate of TCE may be controlled by mass transfer.

1. INTRODUCTION

Volatile organic compounds (VOCs) are widely used in industrial processes and domestic activities. Thus, one of the most important technical issues of recent years is the effective and economical disposal of VOCs in air. Many VOCs are known to be toxic and considered to be carcinogenic. The most significant problem related to the emission of VOCs is centered on the potential production of photochemical oxidants; for example, ozone, aldehyde and peroxyacetyl nitrate. Among these VOCs, TCE especially represents a serious air pollutant for industrial processes or even indoor environments [1]. The PCD of organic compounds using TiO₂ as a catalyst has been proposed as an alternative advanced oxidation process (AOP) for the decontamination of water and air. AOP is initiated from the generation of hole-electron pairs on the

semiconductor upon absorbing UV light with energy equal to or higher than the band gap energy. Electrons and holes photogenerate in the bulk of the semiconductor and move to the particle surface, electrons reduce electron acceptors such as molecular oxygen, and holes can oxidize electron donors including adsorbed water or hydroxide anion to give hydroxyl radicals [2-4].

The PCD of TCE was first reported by Dibble and Raupp [5] to be much faster than that of hydrocarbons and oxygenates, and apparent quantum yield exceeding 100 % have often been measured for TCE degradation. These very high photon efficiencies imply that a chain mechanism is occurring on the TiO_2 surface. In order to determine the kinetics of conversion of trace (0-100 ppm) TCE, Dibble and Raupp [6] systematically investigated the photo-oxidation in air using both a fixed-bed reactor and a fluidized bed reactor. The observed reaction rate was a positive to zero apparent order in TCE and oxygen vapor phase mole fraction, depending on the concentration of each species. Trace water vapor presence was found necessary to maintain photocatalytic catalyst activity for extended periods of time, but higher water vapor levels were strongly inhibitory. Anderson *et al* [7] examined dependency of the TCE photocatalytic degradation rate on the light intensity, feed composition (TCE, O_2 , H_2O) and temperature in a bed reactor packed with TiO_2 pellets. They show that the TCE reaction rate is independent of flow rate when the conversion is less than 10%, which suggests that the external mass transfer is not controlling the reaction rate.

The purpose of the present work is to find the optimum condition for the PCD of gaseous TCE in a continuous flow system with regard to mixing condition by baffle, inlet concentration of TCE, and face velocity of gas flow.

2. EXPERIMENTAL WORK

2.1 Materials and preparation of TiO_2 photocatalyst

All of the chemicals used in the work were reagent-grade. TCE was products of Aldrich (anhydrous, 99%). The photocatalyst was prepared from TiO_2 -sol (STS-01, anatase, 7 nm in diameter, $300 \text{ m}^2 \text{ g}^{-1}$ for specific surface area, Ishihara Sangyo Co.), tetraethyl orthosilicate (TEOS, 98%, Aldrich), dimethoxy dimethyl silane (DMDMS, 95%, Aldrich), isopropyl alcohol (IPA, anhydrous, 99.5%, Aldrich) and nitric acid (65 wt% solution in water, Aldrich). Deionized and doubly distilled water was used for the preparation of the photocatalyst and the generation of water vapor.

The suspension of TiO_2 photocatalyst was prepared through a three-step process as

follows; TEOS (180 g) and DMDMS (90 g) were added to the IPA (900 g) on a vessel connected to a condenser at room temperature (1st step). A solution combined with IPA (900 g), deionized water (45 g) and nitric acid (2.7 g) was dropped in the solution prepared in the first step at a temperature of about 5 °C for 60 min, and stirred for two hours (2nd step). STS-01 (3150 g) was then dropped in a solution combined with IPA (1350 g), deionized water (1350 g) and the solution (2025 g) prepared in the second step at a temperature of about 5 °C for 60 min, and stirred for three hours (3rd step).

A TiO₂ thin-film photocatalyst was formed by the dip-coating method. After filling a Pyrex glass reactor with the TiO₂ photocatalyst suspension, it was removed from the reactor at a constant rate of 5 mm min⁻¹. Then, the reactor coated with TiO₂ was dried at 120 °C for one hour.

2.2 Reactor System

A schematic representation of the experimental set-up of continuous flow system used for performing photocatalytic degradation of TCE at the gas-solid interface is shown in Fig. 1. It includes three parts: generation of gas mixture containing TCE and water vapor, continuous flow photo-reactor, and analytical instrument.

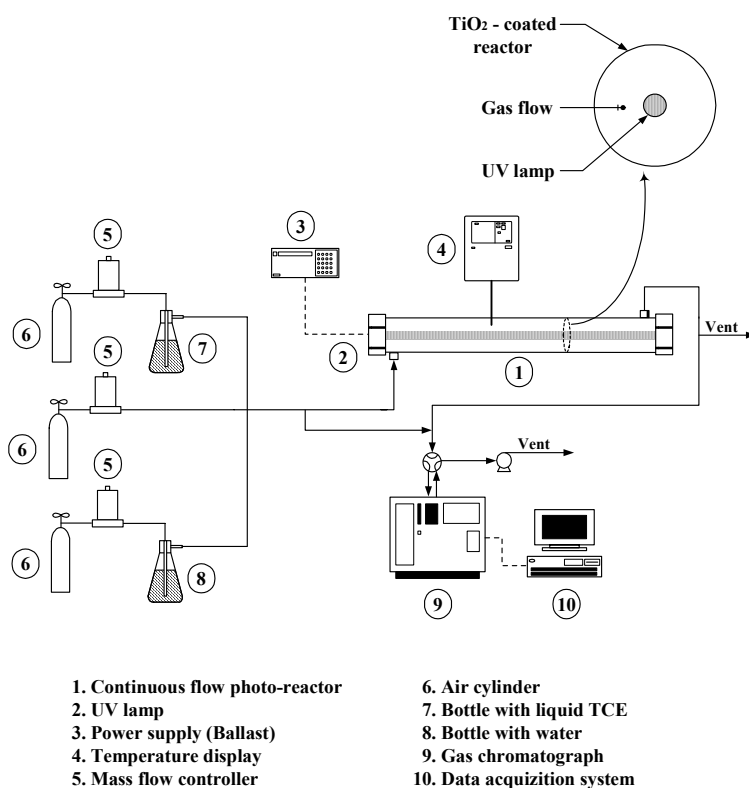


Fig. 1. Schematic diagram of the continuous flow photo-reactor.

A source of main air was supplied from the compressed air cylinders. The gas containing TCE as a model pollutant and water vapor of desired concentration was generated from a bubbler. This bubbler consisted of a reservoir containing the pure (liquid phase) TCE and water, and it was immersed in a thermoregulated bath - circulator (Model TB-85, Shimazu). Temperature of the thermoregulated bath and the gas flow rate determined the concentration of TCE in air. The volumetric flow rate of gas stream was electronically controlled by mass flow controller (Model 8272, Metheson Gas Products). A continuous flow photo-reactor reactor made of Pyrex glass was annular type and had a 1500 mm length, 75 mm inside diameter, and 80 mm outside diameter. This annular type consisted of a Pyrex glass reactor coated on the inner surface with a TiO_2 photocatalyst and UV lamp (15 mm outside diameter, 1553.6 mm length) inserted in the center of the reactor. The UV lamp (Model G64T5L, Light Sources, INC., 65 W) of the germicidal type was used as a light source. The wavelength of UV lamp ranged from 200 to 300 nm with the maximum light intensity at 253.7 nm. The concentration of TCE was measured by a gas chromatograph (Model HP 6890, Hewlett-Packard). The gas chromatograph was equipped with a HP-5 capillary column (Agilent Technologies) of 30 m length, 0.25 μm film thickness and 0.32 mm internal diameter.

In the mean time, the configuration of baffle in the continuous flow photo-reactor is shown schematically in Fig. 2. The aluminum baffle of 70 mm diameter and 0.5 mm thickness was designed with a hole of 20 mm diameter at the center.

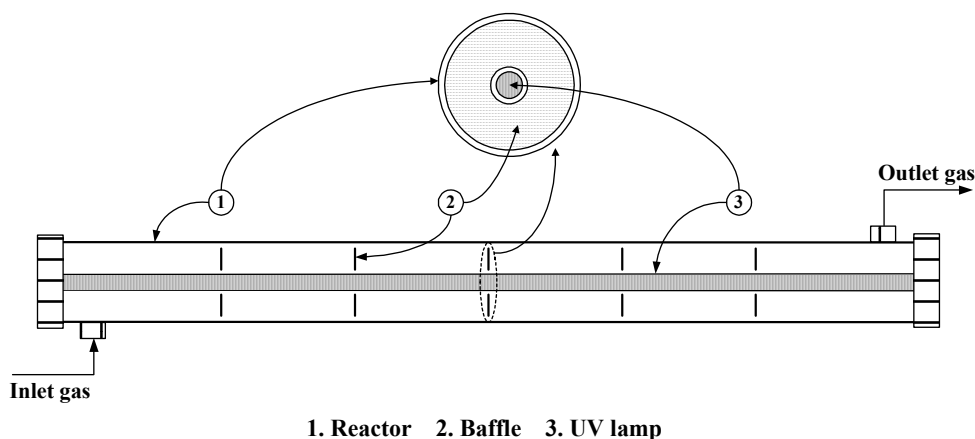


Fig. 2. Configuration of baffles in the continuous flow reactor.

2.3 Experimental methods

Once the gas mixture was introduced, reactor inlet/outlet TCE levels reached adsorption equilibrium. After the adsorption process had reached equilibrium as

indicated by equality between the inlet/outlet TCE concentrations, the UV lamp was turned on. And the concentration of TCE was recorded with the reaction time throughout the test. Influent/effluent gas sample of reactor was moved by a low-flow diaphragm pump (Model SP 600 EC-LC, SP J. Schwarzer GmbH u. Co.) and injected through a six-port external injection GC valve (6890 Valve system, Agilent Technologies) with a 250 μ l automatic sample loop. The sample was then transferred to a gas chromatograph (Model HP 6890, Hewlett-Packard) with pure helium as a carrier gas. Temperatures of the injector and column were maintained at 120 and 200 $^{\circ}$ C, respectively. The flame ionization detector was maintained at 250 $^{\circ}$ C.

In order to examine the effect of installing baffle on residence time distribution (RTD), the RTD function was experimentally determined by pulse injection of a tracer, methane, into the reactor at the time $t = 0$. And then concentration of the tracer in the effluent stream was measured as a function of time. The pure methane (5 cc) was instantaneously injected by a gas tight syringe into the nitrogen feed stream. The outlet concentration of methane was measured by non-dispersed infrared analyzer (Uras 10E, Hartmann & Brown Co.).

3. RESULTS AND DISCUSSION

3.1 Effect of mixing by baffle

The most primary parameter to design the reactor is the reactor size including reactor length or diameter. The annular reactor that the UV lamp was horizontally inserted in the center of the reactor was used in this work. In the annular reactor, length and diameter of the reactor are closely associated with the dimension of UV lamp. Thus, the reactor diameter is one of the essential process variables in reactor design. In the continuous flow process, the most significant parameter to determine the throughput is the gap between the outside of UV lamp and internal surface of the reactor coated with photocatalyst. Expanding the gap to increase the throughput causes the decrease of photon flux and the reduction of mass transfer to the photocatalyst surface in bulk flow. It thereby results in decrease of the PCD efficiency. In order to overcome this problem, the baffle was inserted into the reactor. The baffle affected the flow pattern and RTD of gas flow in the reactor was supposed to improve mass transfer by effective mixing. In consequence, the function of baffle was investigated focusing on RTD.

Figure 3 is RTD functions for the investigation upon the influence by baffle. As can be seen from this figure, as increasing the total flow rate, the centroid of distribution on the time axis moves forward and the spread of distribution is diminished. In other words,

it means that the increase of volumetric flow rate results in decrease of mean residence time and variance.

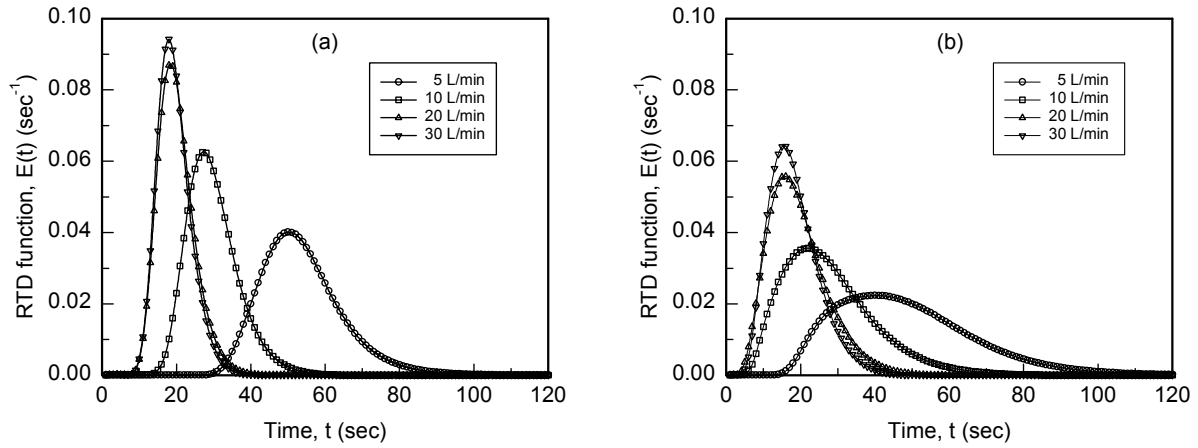


Fig. 3. Residence time distribution profiles according to volumetric flow rate (a) in the absence and (b) presence of baffle.

In order to ascertain the behavior of the reactor depending on the presence of baffles, the values of mean residence time and variance were evaluated. Based on the tanks-in-series model and dispersion model, number of tanks (n) and Peclet number (Pe) were figured out. These values are summarized in Table 1, which means that residence time was smaller with baffles than without baffles, the value of variance was just opposite. In other words, the number of tanks and Peclet number were smaller when the baffles were installed. Conversely, effective mixing could be expected by baffles inducing CSTR behavior in the tubular reactor.

Table 1. Mean residence time, variance, number of ideal tanks, and Peclet number obtained from RTD data in the absence and presence of baffle

Flow rate (L min ⁻¹)	In the absence of baffle				In the presence of baffle			
	t_m (sec)	σ^2 (sec ²)	n	Pe	t_m (sec)	σ^2 (sec ²)	n	Pe
5	53.15	11.21 ²	22.5	48.74	47.62	18.20 ²	6.9	16.92
10	29.31	6.99 ²	17.6	38.84	27.23	12.28 ²	4.9	12.85
20	19.54	5.10 ²	14.7	32.98	18.83	7.83 ²	5.8	14.75
30	18.89	4.54 ²	17.3	38.31	17.74	6.68 ²	7.1	17.46

3.2 Effect of inlet concentration

In the PCD reaction of the continuous flow system, the PCD rate could be evaluated through a differential method of eqn (1) [8-11].

$$-r_A' = \frac{C_{A,in} X_A Q}{S} \quad (1)$$

where, $-r_A'$ ($\text{mol m}^{-2} \text{s}^{-1}$) is the PCD rate; $C_{A,in}$ (mol m^{-3}) is inlet concentration of reactant A; X_A is fractional conversion of reactant A; Q ($\text{m}^3 \text{s}^{-1}$) is total volumetric flow rate; and S (m^2) is geometric area of TiO_2 photocatalyst coated-glass reactor. Many researchers [6-8] reported that the photocatalytic reaction rate increased linearly with inlet concentration of TCE at low inlet concentration, and became constant over a certain inlet concentration, which would obey the typical L-H equation. In order to observe the effect of inlet concentration on the PCD rate of TCE, in the experiment, the PCD rate was evaluated under the operation conditions of 5 to 40 L min^{-1} total volumetric flow rate, $3.83 \times 10^{-1} \text{ mol m}^{-3}$ (1.0 vol. %) water vapor content, and 5.740×10^{-4} to $3.446 \times 10^{-2} \text{ mol m}^{-3}$ inlet concentration (Fig. 4).

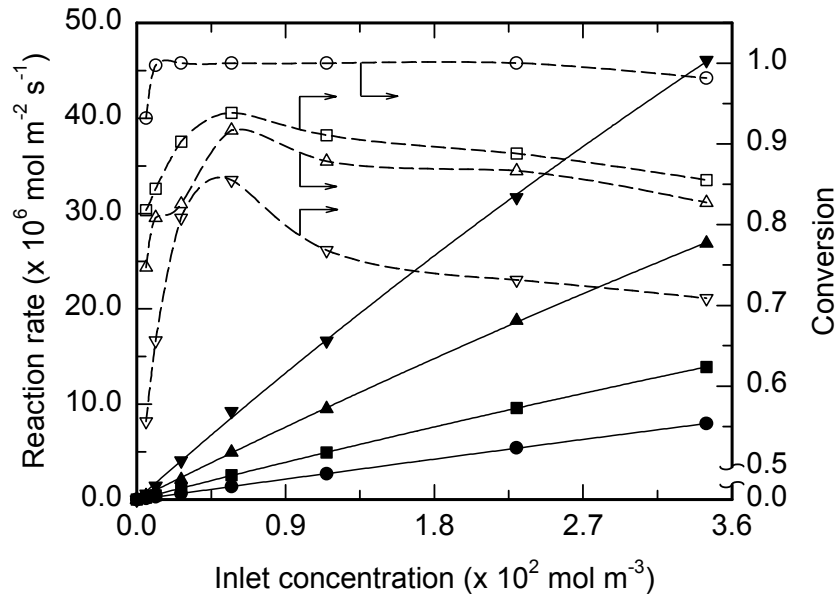


Fig. 4. PCD rate and conversion of TCE according to inlet concentrations ($C_{\text{H}_2\text{O}} = 0.383 \text{ mol m}^{-3}$; UV source: germicidal lamp, light intensity: $6.667 \times 10^{-3} \text{ W cm}^{-2}$; temperature: 45 °C; symbols - circles: 5, squares: 10, triangle up: 20, triangle down: 40 L min^{-1} total flow rate).

As shown in Fig 4, high total volumetric flow rate resulted in higher PCD rate, and the increasing gradient was linear for both low and high total volumetric flow rate. Mass transfer from bulk flow to photocatalyst surface hardly occurs in low total volumetric flow rate. Then, the PCD rate increased linearly with increasing TCE inlet concentration, since mass transfer could be improved due to the increase of molecular diffusion and residence time could be sufficient. Meanwhile, despite a short residence time in high total volumetric flow rate, the photocatalytic degradation reaction of TCE proceeds very rapidly. The photocatalytic degradation rate, after all, continuously increases even in high total volumetric flow rate. Moreover, differing from the former results, Fig 4 does not show the tendency of L-H equation. The PCD rate has continued to increase linearly with TCE inlet concentration. It means that a dilute reactant in low inlet TCE concentration may result in rare possibility of adsorption onto the photocatalyst surface. Thus, increased inlet concentration merely induces much adsorption, eventually leading to increase reaction rate. The PCD reaction pretends to be the first order reaction. Although the surface of photocatalyst is gradually saturated with reactant molecules in high inlet concentration of TCE, the PCD rate increases consistently. It should be due to the rapid chain reaction of chlorine radicals.

3.3 Effect of face velocity

The ratio Q/S in eqn (1) can be defined as a face velocity, which means the flow velocity passing through the reactor [9, 12]. According to former studies, the reaction rate increases linearly with face velocity up to a certain face velocity, then is kept constant. The region of linear increase is generally dominated by mass transfer control, while the constant region is controlled by surface reaction.

The present work was carried out with the variation of face velocity, 0.2358×10^{-3} to $1.8864 \times 10^{-3} \text{ m s}^{-1}$ with a fixed water vapor content, $3.83 \times 10^{-1} \text{ mol s}^{-3}$ (Figs 5 to 7). As shown in these figures, as increasing face velocity, the PCD rate increases linearly. It is due by a dilute phase of TCE in low inlet concentration. Fewer TCE molecules should result in less adsorption. In consequence, high face velocity led to better adsorption by the improved mass transfer effect. Since low inlet concentration could not make a fast saturation of TCE on the surface of photocatalyst, the PCD rate is proportional to the face velocity. Thus it could be defined with mass transfer control region. On the other hand, as previously explained, for high inlet concentration, although the photocatalyst surface is saturated with reactant molecules, TCE participates in a very rapid reaction on the surface. Subsequently mass transfer increases with increasing face velocity. Therefore, it could be found that the region of high inlet concentration was also

controlled by mass transfer.

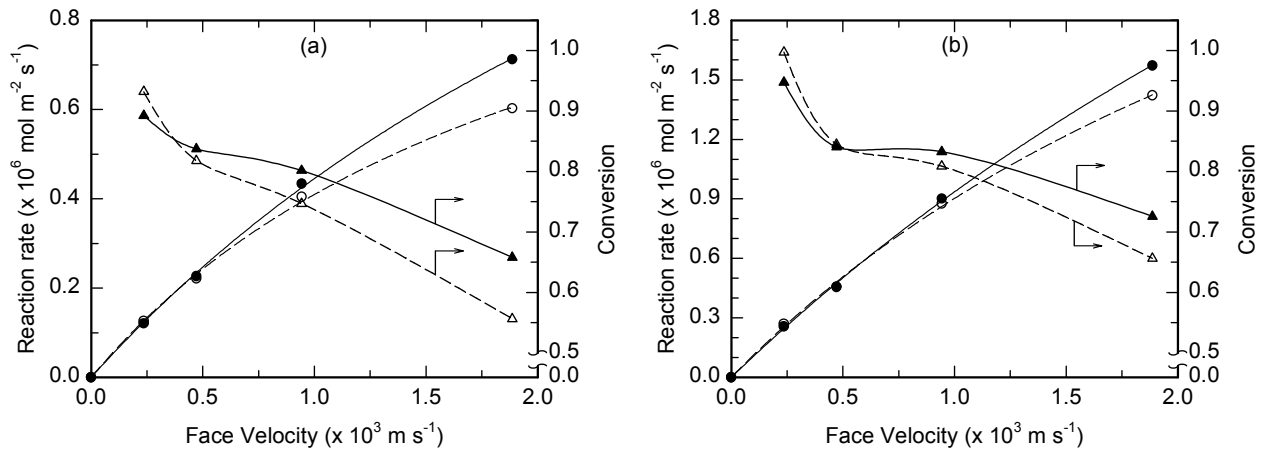


Fig. 5. PCD rate and conversion of TCE according to face velocities (inlet concentration: (a) 5.740×10^{-4} and (b) $1.148 \times 10^{-3} \text{ mol m}^{-3}$; $C_{\text{H}_2\text{O}} = 0.383 \text{ mol m}^{-3}$; UV source: germicidal lamp, light intensity: $6.667 \times 10^{-3} \text{ W cm}^{-2}$; temperature: 45°C ; open symbols: absence of baffle, filled symbols: presence of baffle).

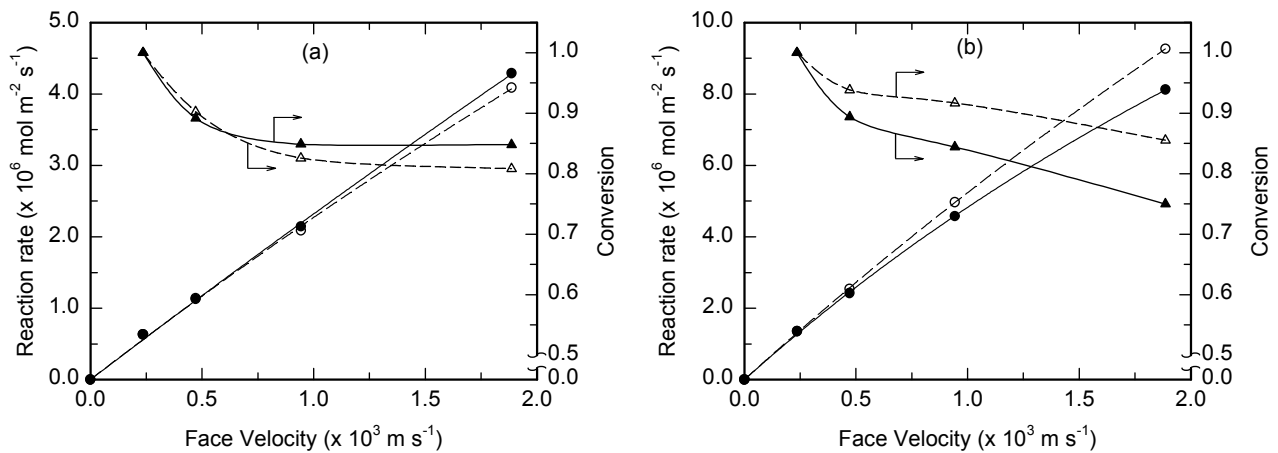


Fig. 6. PCD rate and conversion of TCE according to face velocities (inlet concentration: (a) 2.680×10^{-3} and (b) $5.742 \times 10^{-3} \text{ mol m}^{-3}$; the same other conditions as in Fig. 5).

As already stated, it was found that the effect of mixing could be improved by installing baffle, based on the (tanks-in-series and dispersion model) using RTD data in the existence of baffle. The baffles acted as CSTR behavior in the reactor. Figure 5 and 6 (a) show the effectiveness of baffle. The PCD rate is promoted by using baffles under

the conditions of simultaneous low inlet concentration and high face velocity. The PCD reaction was controlled by mass transfer at low inlet concentration. Thus, baffle aids mixing of gases and improves mass transfer, thereby increasing the PCD rate. Moreover, reactant in high face velocity would pass through without effective contact between reactant and photocatalyst surface due to the decrease of residence time. In consequence, baffles enable the reactants to contact effectively with the photocatalyst surface, and thus the PCD rate can be increased.

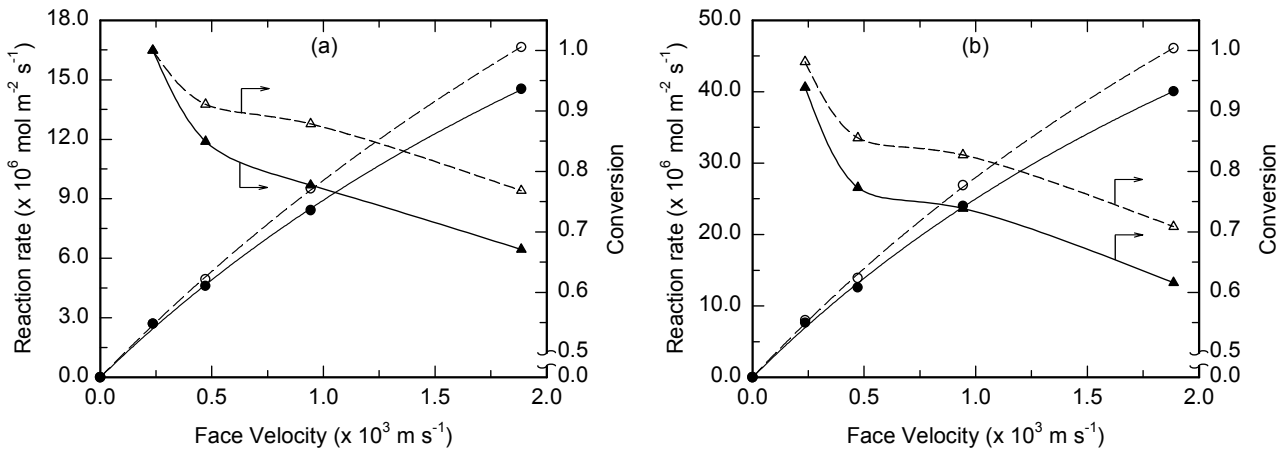


Fig. 7. PCD rate and conversion of TCE according to face velocities (inlet concentration: (a) 1.149×10^{-2} and (b) $3.446 \times 10^{-2} \text{ mol m}^{-3}$; the same other conditions as in Fig. 5).

4. CONCLUSIONS

Conclusions obtained from this work are summarized as follows:

- ☐ The effect of mixing could be improved by installing baffle under the concentrations of simultaneous low inlet concentration and high face velocity, based on the tanks-in-series and dispersion model using RTD data in the existence of baffle. The baffles acted as CSTR behavior in the reactor of tubular type.
- ☐ For the effect of the inlet concentration on the PCD rate of TCE, the rate has continued to increase linearly with TCE inlet concentration.
- ☐ For the influence of face velocity of gas flow, the PCD rate increased with increasing the face velocity in both low and high TCE inlet concentration. Thus, it could be found that the PCD rate of TCE was controlled by mass transfer.

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