

## Degradation of gas-phase trichloroethylene over thin-film TiO<sub>2</sub> photocatalyst in multi-modules reactor

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### ABSTRACT

The present paper examined the photocatalytic degradation (PCD) of gas-phase trichloroethylene (TCE) over thin-film TiO<sub>2</sub>. A large-scale treatment of TCE was carried out using scale-up continuous flow photo-reactor in which nine reactors were arranged in parallel and series. The parallel or serial arrangement is a significant factor to determine the special arrangement of whole reactor module as well as to compact the multi-modules in a continuous flow reactor. The conversion of TCE according to the space time was nearly same for parallel and serial connection of the reactors.

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### 1. Introduction

One of the most important technical issues of recent years is the effective and economical disposal of volatile organic compounds (VOCs) in air. The most significant problem related to the emission of VOCs is centered on the potential production of photochemical oxidants. Among these VOCs, TCE especially represents a serious air pollutant for industrial processes or even indoor environments [1–4].

The PCD of organic compounds using TiO<sub>2</sub> 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 [5–7].

The photocatalytic degradation of TCE was first reported by Dibble and Raupp [8] to be much faster than that of hydrocarbons and oxygenates, and apparent quantum yields exceeding 100% have

often been measured for TCE degradation. These very high photon efficiencies imply that a chain mechanism is occurring on the TiO<sub>2</sub> surface. In order to determine the kinetics of conversion of trace (0–100 ppm) TCE, Dibble and Raupp [9] 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. [10] examined dependency of the TCE photocatalytic degradation rate on the light intensity, feed composition (TCE, O<sub>2</sub>, H<sub>2</sub>O) and temperature in a bed reactor packed with TiO<sub>2</sub> pellets.

The aim of the present work is to determine the special arrangement of whole reactor module. In this work, a large-scale treatment of TCE was carried out using the scale-up continuous flow photo-reactor in which nine reactors were arranged in parallel and series. And the PCD conversion of TCE was compared for the parallel and serial arrangements.

### 2. Materials and methods

#### 2.1. Materials and preparation of TiO<sub>2</sub> photocatalyst

All of the chemicals used in the work were reagent-grade. Acetone was the product of Aldrich (A.C.S. reagent, 99.5%). The pho-

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photocatalyst was prepared from TiO<sub>2</sub>-sol (STS-01, anatase, 7 nm in diameter, 300 m<sup>2</sup> g<sup>-1</sup> 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.

The suspension of TiO<sub>2</sub> 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 TiO<sub>2</sub> thin-film photocatalyst was formed by the dip-coating method. After filling a Pyrex glass reactor with the TiO<sub>2</sub> photocatalyst suspension, it was removed from the reactor at a constant rate of 5 mm min<sup>-1</sup>. Then, the reactor coated with TiO<sub>2</sub> was dried at 120 °C for one hour.

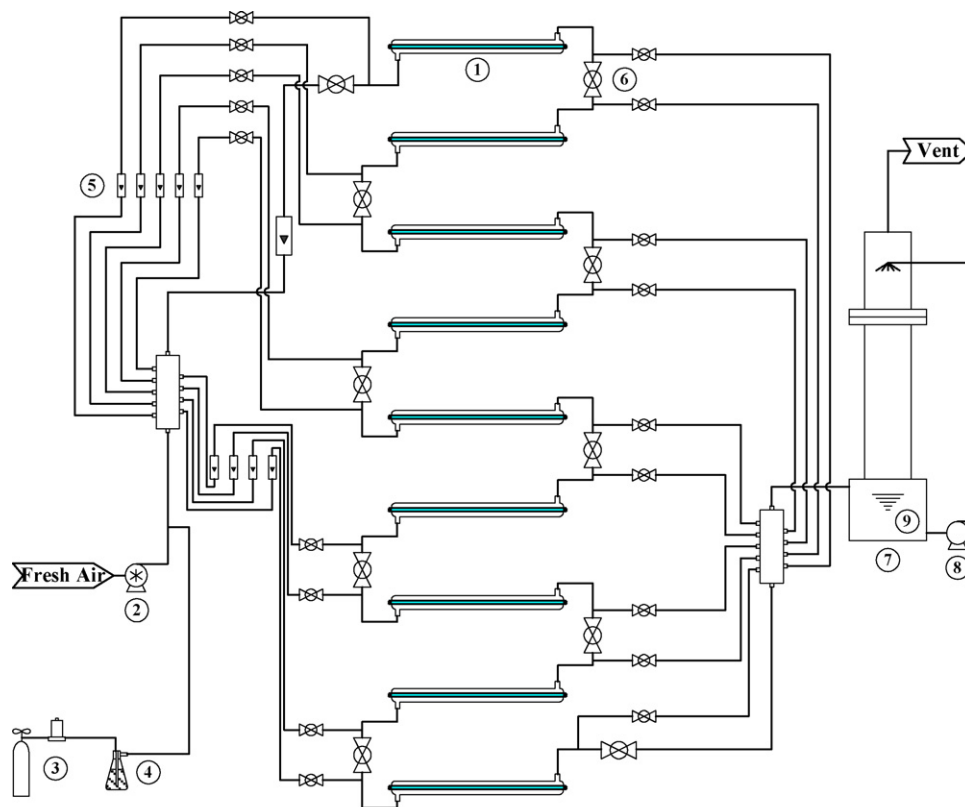
## 2.2. Reactor system

The multi-modules continuous flow reactor, in which nine reactors were arranged in parallel and series, was designed. A schematic

diagram of the experimental set-up is shown in Fig. 1. It includes three parts: generation of a desired gas mixture containing VOC, photocatalytic continuous reactor, and scrubber containing NaOH solution. A source of main air was supplied from blower (Model KJB-1500, KIJEONSA CO.). The volumetric flow rate of gas stream was controlled by flow meter (Model VFA-2", Dwyer Instruments Inc.). The gas mixture containing a desired and stable concentration of TCE was generated using a bubbler. This bubbler consisted of a reservoir containing the pure (liquid phase) TCE and was immersed in a thermoregulated bath—circulator (Model TB-85, Shimazu). The temperature of the thermoregulated bath and the gas flow rate controlled by a mass flow controller (Model 8272, Metheson Gas Products) determined the concentration of TCE in the gas mixture. Relative humidity was measured with a digital hygrometer (Model 485, Dwyer Instruments Inc.). And then, water vapor content in air was converted into relative humidity using psychrometric chart.

An individual photo-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<sub>2</sub> 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



- |  |                  |
|--|------------------|
| 1. Photo-continuous reactor (9- modules) | 6. Ball valve    |
| 2. Blower                                | 7. Scrubber      |
| 3. Air cylinder and MFC                  | 8. Pump          |
| 4. Bottle with liquid VOCs               | 9. NaOH solution |
| 5. Flow meter                            |                  |

Fig. 1. Schematic diagram of the multi-modules continuous flow reactor.

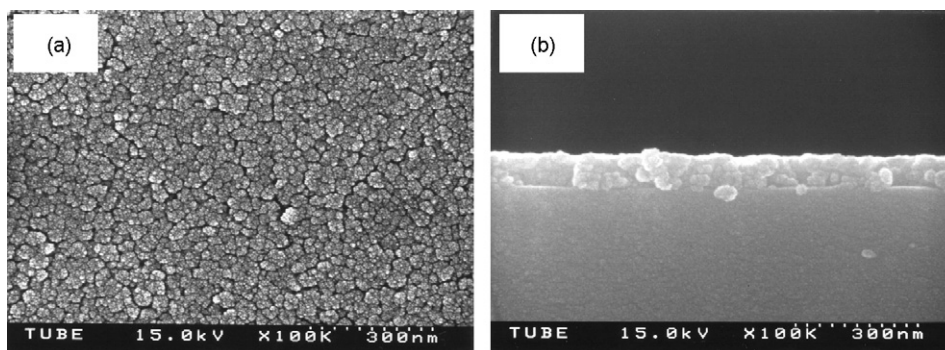


Fig. 2. SEM photographs of (a) top and (b) cross-sectional views of  $\text{TiO}_2$  film on the Pyrex glass reactor

equipped with a HP-5 capillary column (Agilent Technologies) of 30 m length, 0.25  $\mu\text{m}$  film thickness and 0.32 mm internal diameter.

### 2.3. Experimental methods

Once the gas mixture (TCE in air) 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. The concentration of TCE was recorded with the reaction time throughout the test. Influent/effluent gas sample of reactor was 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  $^\circ\text{C}$ , respectively. The flame ionization detector was maintained at 250  $^\circ\text{C}$ .

### 2.4. Characterization of $\text{TiO}_2$ photocatalyst

In this experiment, the  $\text{TiO}_2$  thin-film was prepared by dip-coating method using TEOS, DMDMS, and STS-01 as starting materials. In order to form thin particulate films of  $\text{TiO}_2$  (STS-01) with superior adhesion onto a Pyrex glass support, TEOS and DMDMS as coupling agents were used together.

A uniform and transparent  $\text{TiO}_2$  thin-film with a thickness of about 65 nm was prepared onto an internal surface of a Pyrex glass reactor. Scanning electron microscopy (SEM, Philip SEM-535 M) images are shown in Fig. 2(a and b), which show top and cross-sectional views, respectively. The film consists of small crystalline particles with an average diameter of about 40 nm. Since the average particle size in the  $\text{TiO}_2$  solution was about 7 nm, it is assumed that the particles aggregated during heat treatment. The used  $\text{TiO}_2$  was found to be Anatase by means of X-ray diffraction (Rigaku D/MAX-III (3 kW) diffractometer). As shown in Fig. 3, there are four remarkable peaks at the angles of  $2\theta$ : 25.38, 38.14, 48.04 and 55.02. Specific surface areas of the particles were determined by the BET (Micromeritics ASAP 2100) method. The BET surface area of the prepared  $\text{TiO}_2$  particles was 277  $\text{m}^2\text{g}^{-1}$ .

## 3. Results and discussion

### 3.1. Parallel arrangement

The multi-modules continuous flow reactor, having nine reactors in parallel, was designed for a large-scale treatment. In order to examine the effect of inlet concentration on the photocatalytic degradation rate of TCE, the photocatalytic degradation rate was evaluated under the operating conditions as follows: moisture, 0.345  $\text{mol m}^{-3}$  (0.9 vol.%), equivalent to ambient atmosphere and total volumetric flow rate, 90–450  $\text{l min}^{-1}$  (Fig. 4). As shown in this figure, high total volumetric flow rate resulted in higher photocat-

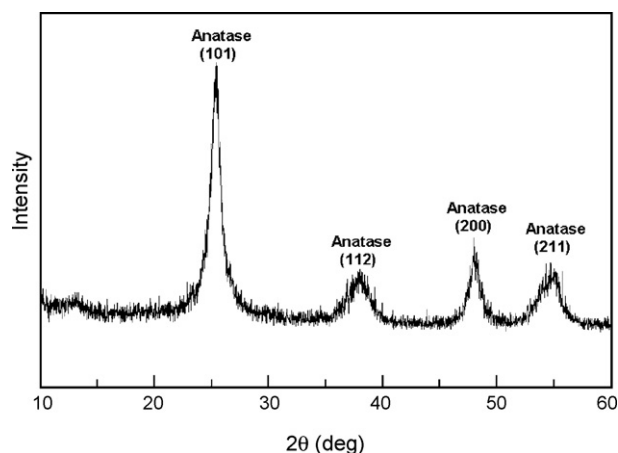


Fig. 3. X-ray diffraction patterns of  $\text{TiO}_2$  film.

alytic degradation 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, as increasing inlet concentration, since mass transfer could be improved due to the increase of molecular diffusion and residence time could be sufficient, the photocatalytic degradation rate increases linearly with TCE inlet concentration. Meanwhile, despite short residence time in high total volumetric flow rate, the photocatalytic degradation reaction of TCE proceeds

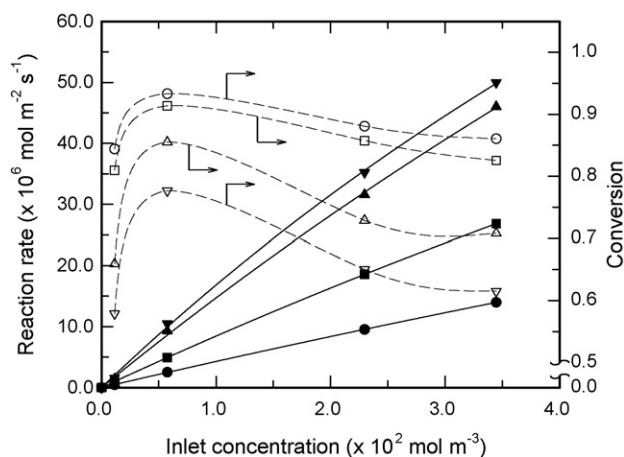
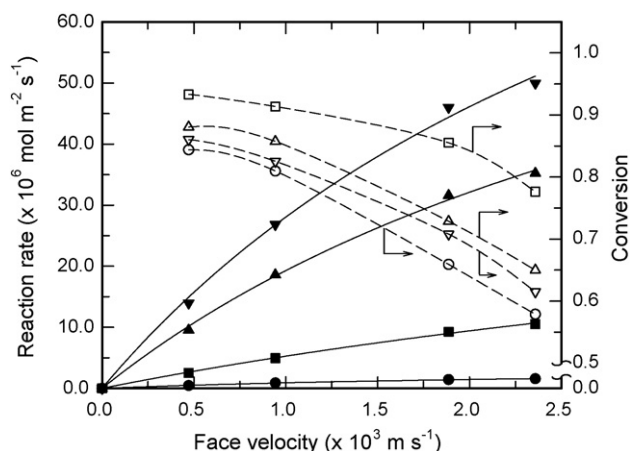


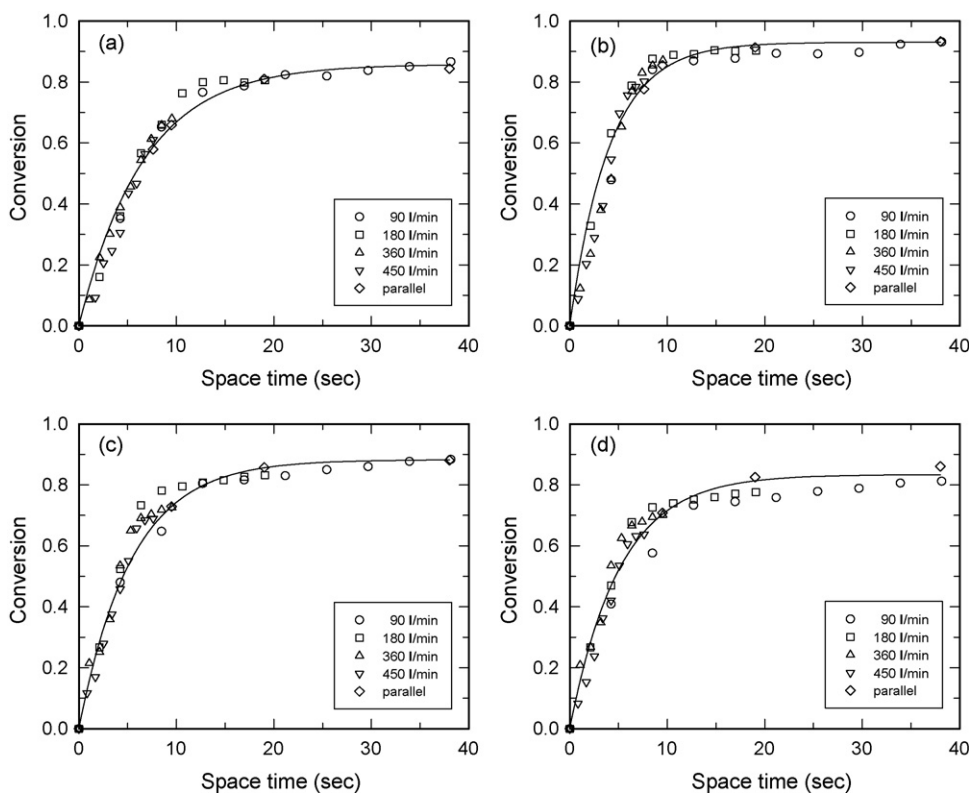
Fig. 4. Photocatalytic degradation rate and conversion of TCE according to inlet concentrations (symbols—circles: 90, squares: 180, triangle up: 360, triangle down: 450  $\text{l min}^{-1}$  volumetric flow rate;  $\text{C}_{\text{H}_2\text{O}} = 0.345 \text{ mol m}^{-3}$ ; UV source: germicidal (254 nm) lamp, light intensity:  $6.667 \times 10^{-3} \text{ W cm}^{-2}$ ; temperature: 45  $^\circ\text{C}$ ).



**Fig. 5.** Photocatalytic degradation rate and conversion of TCE according to face velocities (symbols—circles:  $1.148 \times 10^{-3}$ , squares:  $5.742 \times 10^{-3}$ , triangle up:  $2.297 \times 10^{-2}$ , triangle down:  $3.446 \times 10^{-2}$  mol  $m^{-3}$  inlet concentration;  $C_{H_2O} = 0.345$  mol  $m^{-3}$ ; UV source: germicidal (254 nm) lamp, light intensity:  $6.667 \times 10^{-3}$  W  $cm^{-2}$ ; temperature: 45 °C).

very rapidly. The photocatalytic degradation rate, after all, continuously increases even in high total volumetric flow rate.

To examine the effect of face velocity on the photocatalytic degradation rate of TCE, the photocatalytic degradation rate was evaluated under the operating conditions as follows: moisture, 0.345 mol  $m^{-3}$  (0.9 vol.%), equivalent to ambient atmosphere and TCE inlet concentration,  $1.148 \times 10^{-3}$  to  $3.446 \times 10^{-2}$  mol  $m^{-3}$  (Fig. 5). As can be seen in Fig. 5, as increasing face velocity, the photocatalytic degradation rate increased 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.



**Fig. 6.** Photocatalytic degradation conversion of TCE with each reactor space time at several volumetric flow rate (inlet concentration: (a)  $1.148 \times 10^{-3}$ , (b)  $5.742 \times 10^{-3}$ , (c)  $2.297 \times 10^{-2}$ , and (d)  $3.446 \times 10^{-2}$  mol  $m^{-3}$ ;  $C_{H_2O} = 0.345$  mol  $m^{-3}$ ; UV source: germicidal (254 nm) lamp, light intensity:  $6.667 \times 10^{-3}$  W  $cm^{-2}$ ; temperature: 45 °C).

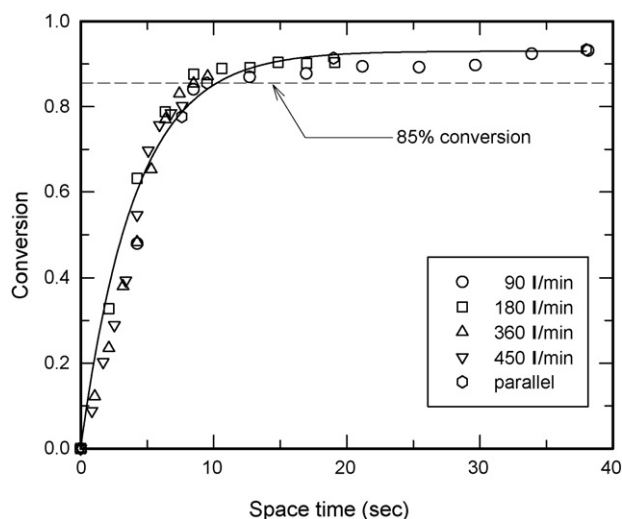
Since low inlet concentration could not make a fast saturation of TCE on the surface of photocatalyst, photocatalytic degradation rate was proportional to the face velocity. Thus, it could be defined with mass transfer control region. On the other hand, as previously stated, for high inlet concentration, although the photocatalyst surface is saturated with reactant molecules, TCE participates in a very rapid reaction on the surface. Subsequently mass transfer increases with the increasing face velocity. Therefore, it could be found that the region of high inlet concentration was also controlled by mass transfer.

### 3.2. Serial arrangement

In order to determine the effect of reactor length, nine reactors were arranged in series, and the outlet concentration of each reactor was measured and the conversion could be evaluated. The test was carried out under the operating condition as follows: moisture, 0.345 mol  $m^{-3}$  (0.9 vol.%), equivalent to ambient atmosphere and total volumetric flow rate, 90–450 l  $min^{-1}$  (Fig. 6(a–d)). Fig. 6 is the conversion for space time of reactant, TCE, in each reactor. As can be seen from these figures, the conversion according to space time does not vary with total volumetric flow rate (i.e., the curves for conversion according to space time follow similar loci with total volumetric flow rate). It concludes that the photocatalytic degradation rate ( $dC_A/d\tau$ ) in the present reactor of PFR type is nothing to do with total volumetric flow rate in case of TCE. Because the photocatalytic degradation of TCE is very rapid due to chain reaction by chlorine radicals, the effect of total volumetric flow rate is not significant.

### 3.3. Comparison of parallel arrangement with serial one

The parallel or serial arrangement is a significant factor to determine the special arrangement of whole reactor module as well as



**Fig. 7.** Estimation of required reactors in serial arrangement for photocatalytic degradation of TCE at several volumetric flow rate (inlet concentration:  $5.742 \times 10^{-3} \text{ mol m}^{-3}$  (150 ppm);  $C_{\text{H}_2\text{O}} = 0.345 \text{ mol m}^{-3}$ ; UV source: germicidal (254 nm) lamp, light intensity:  $6.667 \times 10^{-3} \text{ W cm}^{-2}$ ; temperature:  $45^\circ\text{C}$ ).

**Table 1**

Estimation of required reactors in serial arrangement for photocatalytic degradation of TCE at several volumetric flow rates.

Inlet conc. conversion	Arrangement	Total volumetric flow rate ( $\text{l min}^{-1}$ )	Required reactors
$C_{\text{in}}$ : 150 ppm $X_A$ : 0.85	Serial	90	2–3
		180	3–4
		360	9
		450	9>
	Parallel	360	9

to compact the multi-modules in pilot scale continuous flow reactor. Thus, in this work, the photocatalytic degradation conversion of TCE was compared for parallel and serial arrangement. Since the total volumetric flow rate and total volume of reactor are same for parallel and serial connection of the reactors, the space time must be same, but the linear velocity of the reactant gas is much faster in serial connection than the parallel.

As can be seen in Fig. 6, the conversion of TCE according to the space time was nearly same for parallel and serial connec-

tion of the reactors. In other words, the photocatalytic degradation rate ( $dC_A/d\tau$ ) should not be different in between parallel and serial arrangements. Since the photocatalytic degradation of TCE is very rapid due to chain reaction by chlorine radicals, the effect of the linear velocity of the reactant gas is not significant.

Fig. 7 provides more detailed examples for  $5.742 \times 10^{-3} \text{ mol m}^{-3}$  (150 ppm) of the inlet concentration of TCE. As a result, the arrangement of reactors for TCE is nothing to do with the photocatalytic degradation conversion. Fig. 7 shows the number of reactors required for 85% conversion of 150 ppm TCE. The obtained results are summarized in Table 1.

#### 4. Conclusions

A large-scale treatment of TCE was carried out using the scale-up continuous flow photo-reactor in which nine reactors were arranged in parallel and series. The photocatalytic degradation rate of TCE was compared for parallel and serial arrangement. It concludes that the photocatalytic degradation rate of TCE should not be different in between parallel and serial arrangements. Since the photocatalytic degradation of TCE is very rapid due to chain reaction by chlorine radicals, the effect of the linear velocity of the reactant gas is not significant.

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