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Photo-degradation Characteristics of TCE (Trichloroethylene) in an Annulus Fluidized Bed Photoreactor

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Abstract−The effects of gas velocity, annulus gap on solid (ε_s) and gas phase holdups (ε_g), UV light transmittance and photocatalytic reduction of TCE (trichloroethylene) over TiO_2/silica gel photocatalyst have been determined in an annulus fluidized bed photoreactor. The optimum TCE reduction efficiency exhibits at $\varepsilon_s/\varepsilon_g$ of 0.48, annulus gap of 8 mm and UV light transmittance around 0.20. The most pronounced effects on TCE conversion are found to be gas velocity (U_g) and annular gap in the photoreactor.

Key words: Gas Velocity, Annulus Gap, Annulus-fluidized Bed, TCE Reduction

INTRODUCTION

Several photon induced reaction systems have received considerable attention in both the research and industrial communities in recent years. Some of these reactions were carried out with the aid of solid photocatalyst such as TO_2, ZnO, zeolites [Brucano et al., 1992]. Examples of reactions which can be carried out with these photocatalysts are hydrogen production from the photo-decomposition of water [Khan et al., 1983], and photodegradation of a wide range of toxic pollutants, such as volatile organic compounds (VOCs), NO and SO_2 [Lim et al., 2000a; Lim and Kim, 2002].

In recent years, a fluidized bed has been used for photocatalytic reaction by Yue et al. [1983] who studied the photocatalytic ammonia synthesis using g-alumina catalyst in a fluidized bed reactor since it has uniform light distribution and an immobilizing support. Experiments were performed in a bench scale flat plate fluidized bed for photocatalytic oxidation of trichloroethylene (TCE) in contaminated air streams [Dibble and Raupp, 1992]. Recently, Lim et al. [2000a, b] and Lim and Kim [2002] employed an annulus fluidized bed photocatalytic reactor and determined the effects of various operating variables on decompositions of NO and TCE.

A fluidized bed photocatalytic reactor system has several advantages over a conventional immobilized or slurry-type photocatalytic reactor [Lim and Kim, 2002]. The unique reactor configuration can provide exposure of photocatalyst to UV light and good penetration of the light into the catalyst bed [Lim et al., 2000b]. Based on these photocatalytic reactions, the effects of operating variables on UV light transmission and UV light interactions between photocatalysts should be determined for scale up of the photoreactor system [Iatridis et al., 1990]. Recently, Brucano et al. [1992] reported a comprehensive review of the UV light interaction in heterogeneous photocatalytic reaction system in a flat fluidized bed. They proposed a phenomenological model for simulating the UV light interaction in the photon field and proposed a model to predict the behavior of UV light interaction in the flat fluidized bed photoreactor. Also, Iatridis et al. [1990], Yue et al. [1986] and Brucano et al. [1992] studied the UV light interaction with photocatalyst in flat fluidized bed photocatalytic reactors, but the effect of UV light transmission on photodegradation of TCE has not been reported yet.

Therefore, in the present study, the effects of superficial gas velocity (U_g), annulus gap on phase holdups (ε_s, ε_g), UV light transmittance and photocatalytic reduction of TCE over TiO_2/silica gel photocatalyst have been determined in an annulus fluidized bed photoreactor.

EXPERIMENTAL SECTION

1. Photocatalyst Preparation

Since TiO_2 powder is classified into Geldart C group having poor fluidization property, silica gel (Aldrich, USA) that is transparent to near UV light was used as a support (particle diameter=220-417 μm; surface area=432 $m^2 g^{-1}$) to improve fluidization quality of TiO_2. Precursor solutions for TiO_2 coating on the silica gel were prepared by using titanium ethoxide, ethanol, HCl, hexylene glycole and Milli-Q water as reported by Lim et al. [2000b]. Titanium ethoxide (10 g) and hexylene glycole (5.4 cc) were dissolved in ethanol (100 g). After vigorous mixing at room temperature for 90 minutes, water (0.8 cc) and HCl (0.2 cc) were added to the solution. The molar ratios of water and HCl to the titanium ethoxide were 1 and 0.11, respectively. After this solution was mixed for 90 minutes at room temperature, silica gel (55 g) was added to the aqueous colloidal suspensions of TiO_2. Then, it was dried at 80 °C for 24 hours and calcined at 550 °C for 1 hour. The amount of TiO_2 loading on silica gel was 0.16 g TiO_2/g silica gel.

Physical properties of fresh silica gel and TiO_2-coated silica gel are given in Table 1 and TiO_2/silica gel has irregularly spherical shapes [Lim et al., 2000a]. As can be seen, surface area, pore volume, and mean pore diameter of TiO_2-coated silica gel exhibit somewhat lower values compared with those of fresh silica gel due to pore plugging by impregnation of TiO_2. In addition, from the EDAX, XRD and SEM analyses, it may be found that TiO_2 contents were evenly distributed on the surface of silica gel by the sol-gel method and the

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Table 1. The physical properties of the silica gel and TiO_2/silica gel

	BET surface area	Mean pore diameter	Mean pore volume
Silica gel	432 ($m^2 g^{-1}$)	0.78 (Å)	73 ($cc\ g^{-1}$)
TiO_2/silica gel	389 ($m^2 g^{-1}$)	0.63 (Å)	64 ($cc\ g^{-1}$)

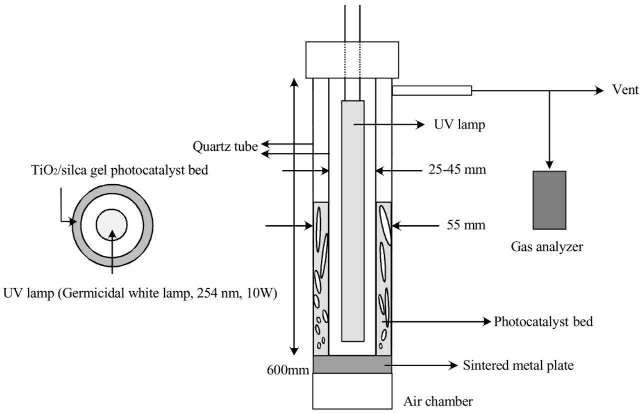

Fig. 1. Schematic diagram of the annulus fluidized bed photoreactor.

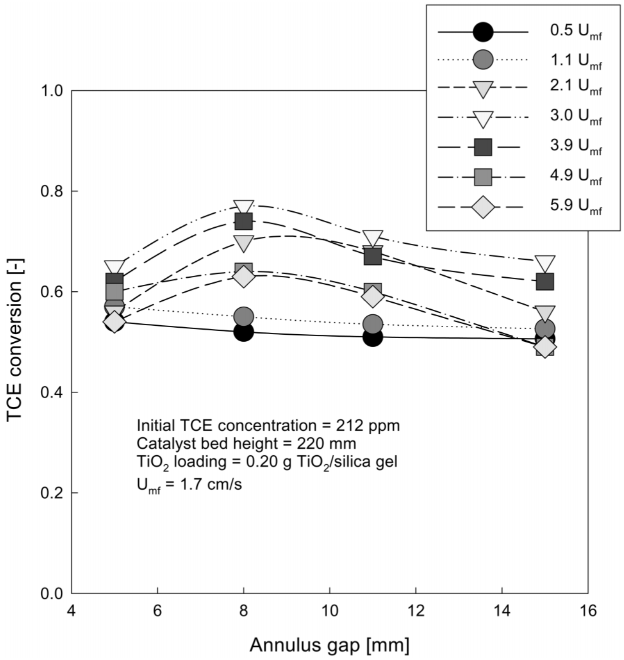

Fig. 2. Effect of annulus gap on the TCE reduction efficiency.

crystal structure of TiO_2 was mainly anatase.

2. Annulus Fluidized Bed Photoreactor

The annulus fluidized bed photoreactor is shown in Fig. 1, where one of four different diameters (25, 33, 39, 45 mm-OD×550 mm-high) of quartz glass tubes was placed at the center of a larger quartz glass tube (55 mm-ID×600 mm-high) in order to vary the annulus gap. A sintered metal plate was used as a gas distributor to provide uniform fluidization of TiO_2/silica gel photocatalyst. To minimize loss of light irradiation and to improve utilization of reflected and deflected lights, a hexagonal mirror box surrounded the photoreactor and the germicidal white light UV lamp (8 W, Sankyo Denki Japan, G8T8) was affixed at the wall of the mirror box. In addition, a germicidal white light UV lamp (10 W, Sankyo Denki Japan, G10T10) was installed inside of the smaller quartz tube for effective UV light irradiation. The flow rate of reactant gas (99.999% He, 247 ppm TCE/He balance, 375 ppm CO/He balance) to the reactor was regulated by a flowmeter (Matheson 603,602, U.S.A.) to match a suitable TCE concentration.

The minimum fluidization velocity (U_{mf}) of TiO_2/silica gel photocatalyst was determined by pressure drop and expanded bed height in the bed with variation of U_g [Lim et al., 2000a].

Photo-illumination was provided with six germicidal white light lamps (8 W, Sankyo Denki, Japan, G8T8). Wavelength of the white lamp ranged from 200 to 300 nm with the maximum light intensity at 254 nm. The light intensity was measured by the UV radiometer (VLX-3W, Wavelength-254 nm, Cole-Parmer). The concentration of TCE was measured by gas chromatography (HP 6890) II by using an auto-sampling valve system (Valco instrument Inc., A60).

RESULTS AND DISCUSSION

1. Effect of the Annulus Gap on TCE Reduction Efficiency

The effect of annulus gap (5, 8, 11, 15 mm) on the TCE reduction efficiency over TiO_2/silica gel photocatalyst is shown in Fig. 2 where the TCE reduction efficiency for species i is defined as

$$\text{TCE reduction efficiency} = \frac{C_{o,i} - C_{f,i}}{C_{o,i}} \qquad (1)$$

where $C_{o,i}$ and $C_{f,i}$ are the initial and final concentrations of species i, respectively.

As can be seen, TCE reduction efficiency exhibits the maximum values at the annulus gap of 8 mm and decreases slightly with a further increase in the annulus gap at U_g=2.0-4.9 U_{mf}. With decreasing the annulus gap, bubbles can easily touch both sides of the walls of the reactor. However, it is rather difficult to have good fluidization with the proper amount of catalyst since TiO_2/silica gel photocatalyst becomes cohesive at the wall of glass tube due to the change of catalyst surface properties through UV light irradiation [Sopyan et al., 1996]. Also, the effective volume of the photoreactor decreases with decreasing the annulus gap. With a further increasing in the annulus gap, TCE reduction efficiency slightly decreases due to decrease of UV light transmission through bubbles into the reactor. Since TCE reduction efficiency is not a function of annulus gap at a fixed bed condition (U_g=0.5 U_{mf}), the efficiency is comparable to the annular flow type photoreactor [Lim and Kim, 2002]. The optimum annulus gap for the maximum TCE reduction efficiency is found to be 8 mm at U_g=2.0-4.9 U_{mf} and 5 mm at U_g=1.3 U_{mf}. Therefore, in the present study, an annulus gap of 8 mm was selected for all the experimental conditions. The optimum annulus gap shifts to higher values due to the increase of bubble size to touch the both sides of the reactor walls with increasing U_g. Thus, the annulus gap is an important parameter to govern proper bubble size for light transmission to increase TCE reduction efficiency over TiO_2/silica gel photocatalyst in the present study as found previously [Iatridis et al., 1990].

2. Effect of an Annulus Gap on Gas Holdup (ε_g)

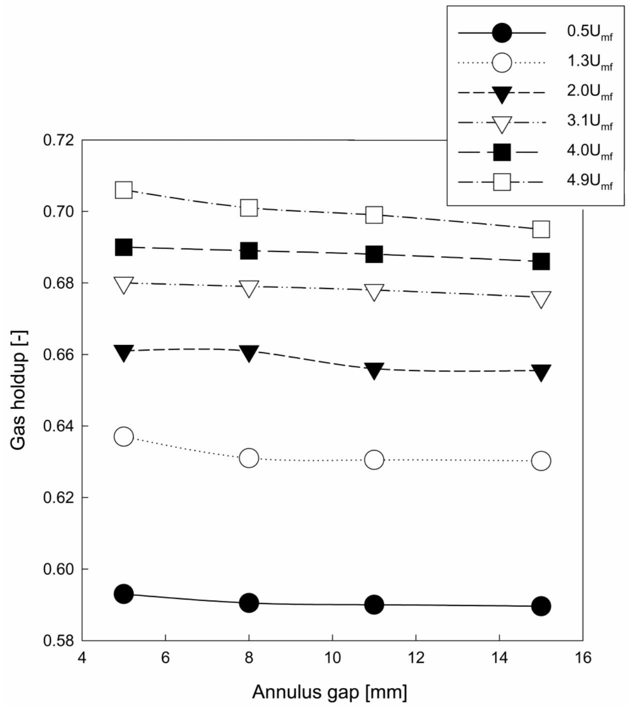

Fig. 3. Effect of annulus gap on gas holdup at different superficial gas velocities.

The effect of annulus gap on gas holdup (ε_g) with variation of superficial gas velocity (U_g) is shown in Fig. 3. As can be seen, ε_g decreases somewhat with increasing annulus gap at a given U_g due to smaller bubble size. In addition, at lower U_g, decreasing rate of ε_g is less pronounced compared with that at higher U_g. As expected, ε_g is mainly governed by the annulus gap and U_g. However, it can be seen in Fig. 3 that U_g plays a major role to govern ε_g than the annulus gap in the annulus fluidized bed photoreactor.

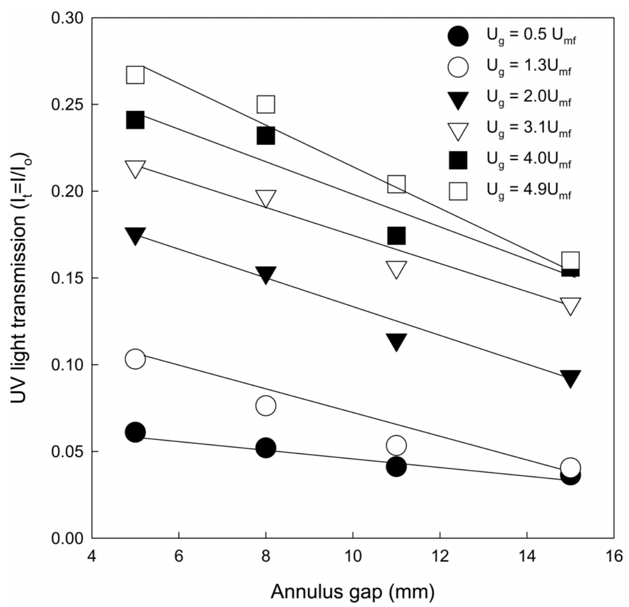

Fig. 4. UV light transmittance as a function of annulus gap at different superficial gas velocities.

3. The Effect of Annulus Gap on UV Light Transmittance

The effect of annulus gap on UV light transmittance in the reactor is shown in Fig. 4 where UV light transmittance is defined as

$$\text{UV light transmittance } (I_t) = \frac{I}{I_o} \tag{2}$$

where I and I_o are fraction of UV light intensity transmitted through the reactor and fraction of initial UV light intensity, respectively, and it can be changed with varying an annulus gap and a superficial gas velocity [Brucano et al., 1992].

As can be seen, UV light transmittance gradually decreases with increasing annulus gap at a given U_g due to the decrease of bubble size in the annulus fluidized bed. This trend is comparable with the data of Yue et al. [1986] who determined voidages of bubble and dense phases in thin two-dimensional fluidized beds.

4. Reduction Efficiency of TCE as a Function of Phase Hold-up Ratio ($\varepsilon_s/\varepsilon_g$)

The relationship between $\varepsilon_s/\varepsilon_g$ and photocatalytic activity over TiO_2/silica gel as the bed material in the photoreactor is shown in Fig. 5. As can be seen, the TCE reduction efficiency over TiO_2/silica gel photocatalyst exhibits a maximum value at $\varepsilon_s/\varepsilon_g$ around 0.48 where the UV light transmission into the interior of the reactor through larger bubbles and mixing of TiO_2/silica gel and TCE gas seems to be at the maximum condition. Thereafter, TCE reduction efficiency decreases with a further increase in $\varepsilon_s/\varepsilon_g$ due to bypassing of TCE gas through larger bubbles and reduction of residence time of TCE gas in the reactor [Lim et al., 2000a].

The optimum phase holdup ratio ($\varepsilon_s/\varepsilon_g$) for the optimum TCE reduction in the present study is higher than that of Yue et al. [1983] who studied the photocatalytic ammonia synthesis using γ-alumina catalyst in a fluidized bed reactor. This result may come from the better fluidization [Dibble and Raupp, 1992] of silica gel particles coated with TiO_2 by the sol-gel method and better transmit of UV light through the transparent silica gel particles compared with γ-alumina catalyst. Therefore, it can be claimed that the present an-

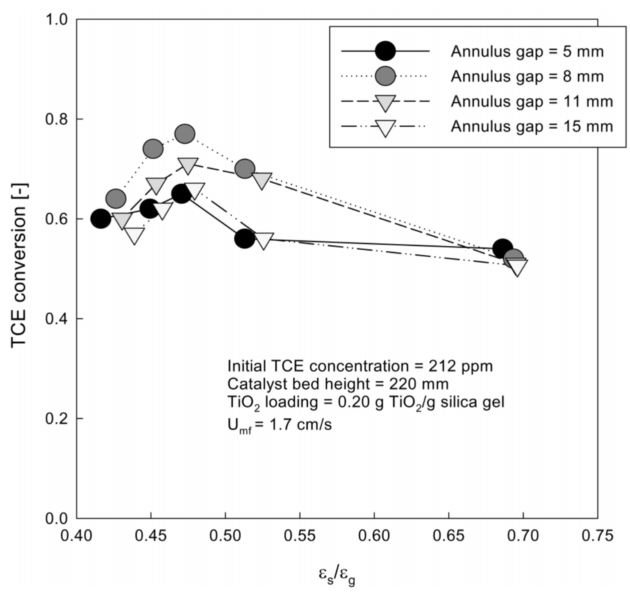

Fig. 5. Reduction efficiency of TCE as a function of $\varepsilon_s/\varepsilon_g$ with different annulus gaps.

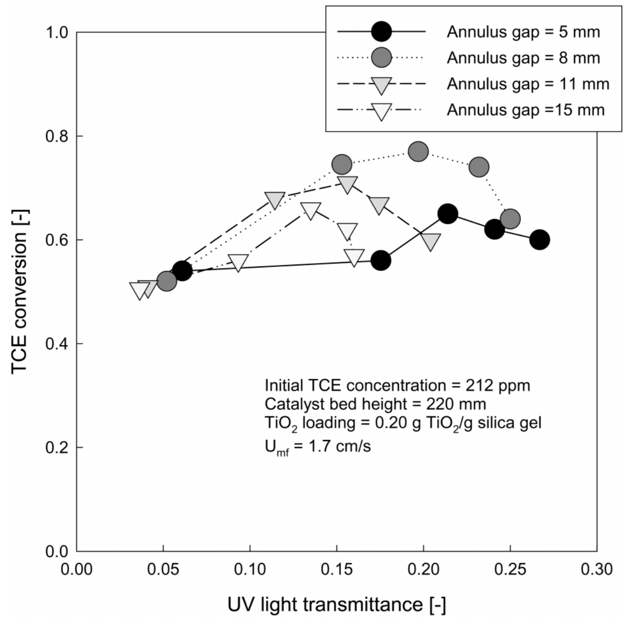

Fig. 6. Reduction efficiency of TCE as a function of UV light transmittance with different annulus gaps.

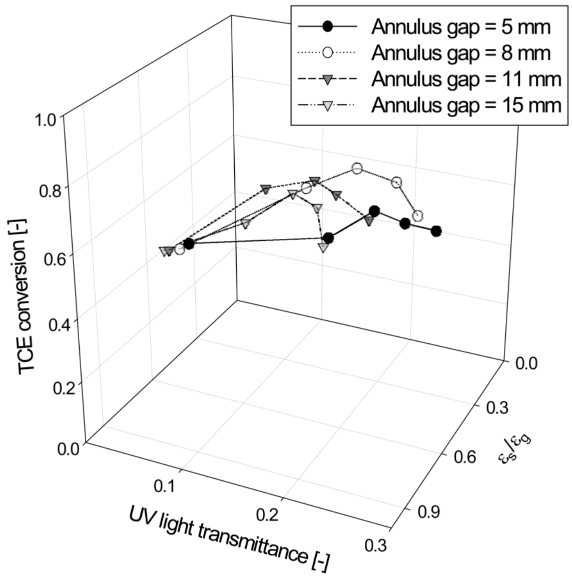

Fig. 7. Three-dimensional diagram for TCE reduction efficiency as a function of $\varepsilon_s/\varepsilon_g$ and UV light transmittance with a variation of annulus gap.

nulus fluidized bed photoreactor of TiO_2/silica gel is an effective reactor tool for the photocatalytic reduction of TCE with an efficient utilization of photon energy.

5. Reduction Efficiency of TCE as a Function of UV Light Transmittance

The TCE reduction efficiency over TiO_2/silica gel photocatalyst as a function of the UV light transmittance is shown in Fig. 6. As can be seen, TCE reduction efficiency exhibits the maximum values at the UV light transmittance around 0.20 due to the increase of UV light penetration through bubbles and it decreases with a further increase in UV light transmittance due to the reduction of UV light adsorption on the photocatalyst [Yue et al., 1986; Brucano et al., 1992] and maximum value of UV light transmittance shifts to lower value with increasing an annulus gap due to the change of contact between TiO_2/silica gel-TCE-UV light through the difference of UV light transmittance. In addition, with a further increase in the annulus gap from 5 to 15 mm, UV light transmittance somewhat decreases due to attenuation of UV light energy by the Lambert-Beer type law [Brucano et al., 1992]. Therefore, it can be concluded that UV light transmittance is an important factor that affects the performance of annulus fluidized bed photoreactor as reported previously by Rizzuti and Yue [1983].

6. Reduction Efficiency of TCE as a Function of $\varepsilon_s/\varepsilon_g$ and UV Light Transmittance

Three-dimensional diagram for TCE reduction efficiency as a function of $\varepsilon_s/\varepsilon_g$ and UV light transmittance with a variation of annulus gap is shown in Fig. 7. As can be seen, the reduction efficiency exhibits a maximum value at $\varepsilon_s/\varepsilon_g$ around 0.48 at the UV light transmittance around 0.20 and the annulus gap around 8 mm. Therefore, it may be claimed that the most pronounced effects of experimental variables on $\varepsilon_s/\varepsilon_g$ and UV light transmittance which affect the performance of an annulus fluidized bed photoreactor are found to be gas velocity and annulus gap for the optimum contact between photocatalysts, gas and UV light through bubbles in the photoreactor and good penetration of UV light into the photocatalyst bed [Iatridis et al., 1990; Brucano et al., 1992; Rizzuti and Yue, 1983; Yue et al., 1986]. These optimum design variables may provide the basic design data for the practical application of an annulus fluidized bed photoreactors.

CONCLUSION

The photocatalytic reduction characteristics of TCE over TiO_2/silica gel photocatalyst have been determined in an annulus fluidized bed photoreactor. The most pronounced effects on TCE conversion are found to be gas velocity and annular gap that vary phase holdups (ε_s, ε_g) and UV light transmittance for the optimum contact between the catalyst and the reactant gases with good penetration of UV light through bubbles in the photocatalyst bed. An annulus fluidized bed photoreactor is an effective tool for higher TCE reduction over TiO_2/silica gel with efficient utilization of photon energy.

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NOMENCLATURE

$C_{o,i}$: initial concentration of species i [ppm]
$C_{f,i}$: final concentration of species i [ppm]
W : mass of TiO_2 photocatalyst [g]
H : catalyst bed height [mm]
V : volumetric flow rate of TCE [$cc \cdot min^{-1}$]
U_g : superficial gas velocity [$cm \cdot s^{-1}$]
U_{mf} : minimum fluidizing velocity [$cm \cdot s^{-1}$]

I : UV light intensity transmitted through the reactor [$\mu W \cdot cm^{-2}$]
I_o : initial UV light intensity [$\mu W \cdot cm^{-2}$]
I_t : UV light transmittance [-]
X : TCE reduction efficiency [-]
ε_g : gas holdup [-]
ε_s : solid holdup [-]

REFERENCES

Brucano, A., Iatridis, D., Rizzuti, L. and Yue, P. L., "Modelling of Light Transmittance and Reflectance in Flat Fluidized Photoreactor," *Can. J. Chem. Eng.*, **70**, 1063 (1992).

Dibble, L. and Raupp, G., "Fluidized-Bed Photocatalytic Oxidation of Trichloroethylene in Contaminated Air Streams," *Environ. Sci. Technol.*, **26**, 492 (1992).

Iatridis, D., Yue, P. L., Rizzuti, L. and Brucano, A., "The Adsorption of Light Energy in Flat Fluidized Photoreactors," *Chem. Eng. J.*, **45**, 1 (1990).

Khan, F., Yue, P. L., Rizzuti, L. and Augugliaro, V., "Photoassisted Water Cleavage and Nitrogen Fixation over Titanium Exchanged Zeolites," *Ind. Eng. Chem. Res.*, **22**, 238 (1983).

Lim, T. H., Jeong, S. M., Kim, S. D. and Janos, G., "Photocatalytic Decomposition of NO by TiO_2 Particles," *J. Photochem. Photobiol. A: Chem.*, **134**, 209 (2000a).

Lim, T. H., Jeong, S. M., Kim, S. D. and Janos, G., "Degradation Characteristics of NO by Photocatalysis with TiO_2 and CuO/TiO_2," *React. Kinet. Catal. Lett.*, **71**, 223 (2000b).

Lim, T. H. and Kim, S. D., "Photocatalytic Degradation of Trichloroethylene over TiO_2/SiO_2 in an Annulus Fluidized Bed Reactor," *Korean J. Chem. Eng.*, **19**, 1072 (2002).

Sopyan, I., Mitsuru, W., Sadao, M., Hashimoto, K. and Fujishima, A., "Efficient TiO_2 Powder and Film Photocatalysts with Rutile Crystal Structure," *Chem. Lett.*, **69** (1996).

Rizzuti, L. and Yue, P. L., "The Measurement of Light Transmission through an Irradiated Fluidized Bed," *Chem. Eng. Sci.*, **38**, 1241 (1983).

Yue, P. L., Khan, F. and Rizzuti, L., "Photocatalytic Ammonia Synthesis in a Fluidized Bed Reactor," *Chem. Eng. Sci.*, **38**, 1893 (1983).

Yue, P. L., Rizzuti, L. and Augugliaro, V., "Bubble Phase Voidage and Dense Phase Voidage in Thin Two-Dimensional Fluidized Beds," *Chem. Eng. Sci.*, **41**, 171 (1986).