Photocatalytic Degradation of Trichloroethylene over TiO$_2$/SiO$_2$ in an Annulus Fluidized Bed Reactor

Tak-Hyoung Lim and Sang-Done Kim[†]

Department of Chemical and Biomolecular Engineering, Energy and Environment Research Center,
Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea

Abstract−The effects of superficial gas velocity (U$_g$), wavelength and intensity of ultraviolet (UV) light, oxygen and H$_2$O concentration on the photocatalytic degradation of TCE (Trichloroethylene) over TiO$_2$/SiO$_2$ catalyst have been determined in an annulus fluidized bed photoreactor. The key factor in determining the performance of the annulus fluidized bed photoreactor is found to be an optimum superficial gas velocity (U$_g$) that provides the optimum UV light-transmit through the proper size of bubbles in the photoreactor. The degradation efficiency of TCE increases with light intensity but decreases with wavelength of the UV light and H$_2$O concentration in the fluidized bed of TiO$_2$/silica-gel photocatalyst. The optimum concentration of O$_2$ for TCE degradation is found to be approximately 10%. The annulus fluidized bed photoreactor is an effective tool for high TCE degradation with efficient utilization of photon energy.

Key words: TCE Degradation, TiO$_2$/SiO$_2$, Fluidized Bed Photoreactor

INTRODUCTION

Recently, increments of the greenhouse effect as well as the environmental concerns on large-scale emission of toxic materials into the atmosphere and water require new chemical processes for clean and safe reduction of such toxic materials. Trichloroethylene (TCE) is an especially harmful atmospheric pollutant that causes acid rain, photochemical smog, and the formation of peroxy acetyl nitrates (PAN) [Zhang et al., 2001].

Various processes, such as incineration, adsorption on activated carbon, air bubbling, condensation and bio-filtration methods are under operation to remove TCE from stationary sources [Izumi et al., 1980]. However, the costs of construction and operation of such methods and energy consumption have been estimated to be very high. Therefore, a novel technology is required to overcome these drawbacks and many studies have been reported in the literature [Yamazaki et al., 1993; Tanguat et al., 1989; Nimlos et al., 1993].

In recent years, attention has been focused on gas-phase photocatalysis since TCE can be decomposed much faster in gas phase than in aqueous phase [Tanguat et al., 1989]. In addition, gas phase photocatalytic degradation of TCE has been studied to elucidate its reaction mechanism. Yamazaki et al. [1993] investigated the photocatalytic degradation of gas-phase TCE to CO$_2$ and HCl in a packed-bed reactor of highly porous TiO$_2$ pellets. Nimlos et al. [1993] found that the main byproducts of TCE photodegradation are Cl$_2$, HCl, CO, CO$_2$, Cl$_2$CO, and Cl$_2$HCC(O)Cl from the gas phase FTIR study.

As a photocatalyst, TiO$_2$ has attracted extensive interest because it has various attractive properties such as nontoxicity, high stability, low cost, and highly reactive catalyst at low temperature for chemical waste remediation. The basic principle of such photocatalysis

involves migration of photo-generated electrons (e$^-$) and holes (h$^+$) to the surface of TiO$_2$ which serve as the redox reactants, leading to surface catalyst reactions [Zhang et al., 2001].

When a photocatalytic reaction takes place in a gas-solid reactor, it is necessary to achieve both exposures of photocatalysts to UV light and good contact between reactants and photocatalyst. A fluidized bed photoreactor not only brings more contact of photocatalyst and gas but also enhances UV light penetration through bubbles compared to a packed bed reactor in which UV light cannot penetrate into the interior of the reactor [Yue and Khan, 1983]. Therefore, it is important to design a fluidized bed photoreactor having higher light throughputs and lower pressure drop.

Therefore, in the present study, the effects of superficial gas velocity (U$_g$), wavelength and intensity of ultraviolet (UV) light, oxygen and H$_2$O concentrations on the photocatalytic degradation of TCE (Trichloroethylene) over TiO$_2$/SiO$_2$ catalyst have been determined in an annulus fluidized bed reactor.

EXPERIMENTAL

1. Photocatalyst Preparation

Since TiO$_2$ powder is classified into Geldart C group having poor fluidization characteristics [Lim et al., 2000b], silica gel (Aldrich, USA) that is transparent to near UV light (particle diameter=220-417 μm; surface area=432 m^2/g) was used as a support 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. [2000a]. 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

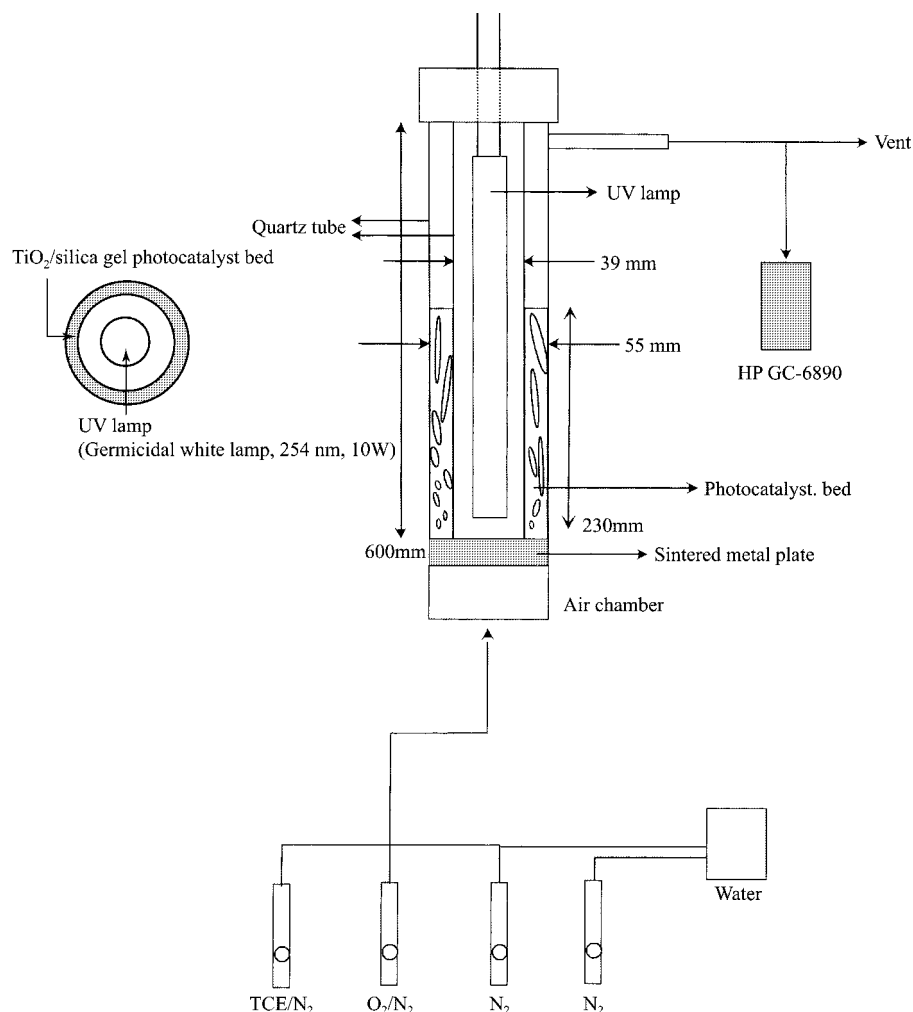[†]To whom correspondence should be addressed.
E-mail: kimsd@kaist.ac.kr

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

was dried at 80 °C for 24 hours and calcined at 550 °C for 1 hour.

2. Annulus Fluidized Bed Photoreactor

As shown in Fig. 1, a small quartz glass tube (39 mm-O.D×600 mm-high) was located at the center of a larger quartz glass tube (55 mm-ID×600 mm-high) to form the annular shape. A sintered metal plate was used as a distributor to provide uniform fluidization of TiO₂/silica gel photocatalyst. To minimize loss of light irradiation and to improve utilization of reflected and deflected light, a hexagonal mirror box surrounded the photoreactor and the white & black light UV lamp (8 W, Sankyo Denki Japan, G8T8, B8T8) was affixed at the wall of the mirror box. In addition, a white & black light UV lamp was installed inside of the smaller quartz tube for effective UV light irradiation. Photoillumination was provided with six lamps (8 W, Sankyo Denki Japan, F8T8-BLB) and six germicidal white light lamps (8 W, Sankyo Denki Japan, G8T8-BLB). Wavelength of the fluorescent black light lamp ranged from 300 nm to 400 nm, with the maximum light intensity at 365 nm and wavelength of the white light lamp ranged from 200 nm to 300 nm with the maximum light intensity at 254 nm. The light intensity was measured by the UV radiometer (VLX-3 W, Wavelength-254 nm, Cole-Parmer).

The concentrations of TCE were measured by gas chromatography (HP 6890 II) by using an autosampling valve system (Valco instrument Inc., A60), and the minimum fluidization velocity (U_{mf}) of TiO₂/silica gel photocatalyst was determined by pressure drop and the expanded bed height with variation of U_g [Lim et al., 2000a].

RESULTS AND DISCUSSION

To assess the photocatalytic degradation of TCE, a series of experiments by intermittent irradiation was performed by switching on-off the UV light lamp. As can be seen in Fig. 2, there is no sign of TCE degradation for 5 minutes in the UV lamp-off condition. After the light is switched on, the concentration of TCE rapidly drops until reaching steady state around 10 minutes. After the UV light is switched off, TCE concentration increases immediately to the original value and remains without any decrease. By turning on the UV lamp again, there is similar photodegradation as of the previous one, reaching steady state about 10 minutes. By repeating the operation again, the same results can be obtained. Therefore, we may conclude that the decrease of TCE concentration is caused by the photocatalytic degradation of TCE in the presence of TiO₂/silica gel photocatalyst with UV light irradiation. In addition, the rapid rise of TCE concentration while without the UV light irradiation indicates that the free radical generated by the photoreaction pri-
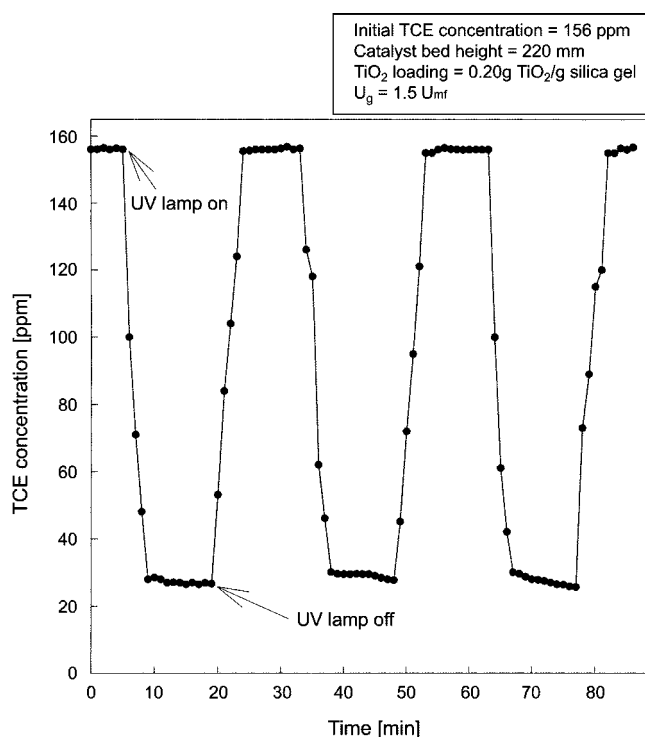
Fig. 2. TCE concentration profile as a function of a reaction time.

Fig. 4. Effect of superficial gas velocity on TCE conversion.

marily underwent surface reaction. In one theory [Wang et al., 1998], if the free radical transfer is the primary reaction, the free radicals would diffuse into the gas phase; thus the reaction would sustain for a while as the UV light went off. However, the rapid rises of TCE concentration after switching off UV light indicate that the free radical transfer mechanism is insignificant.

The effect of TiO_2/SiO_2 ratio on TCE conversion is shown in Fig. 3. As can be seen, TCE conversion in the photocatalytic degrada-
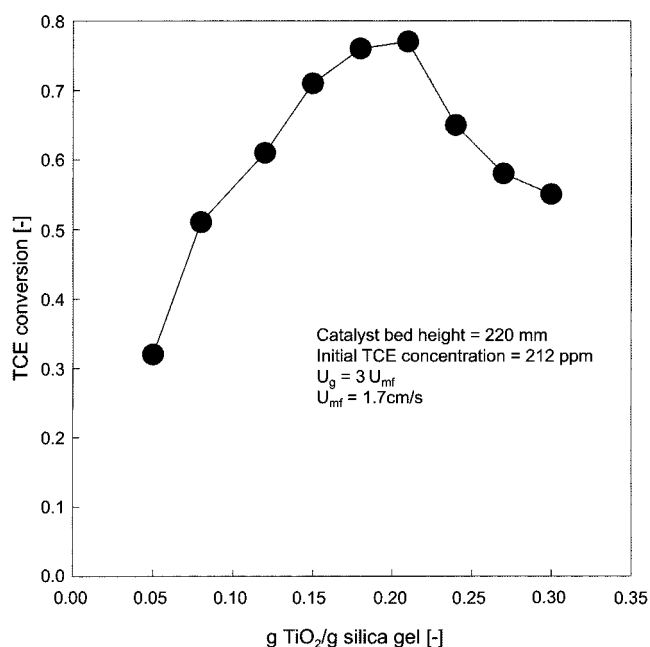

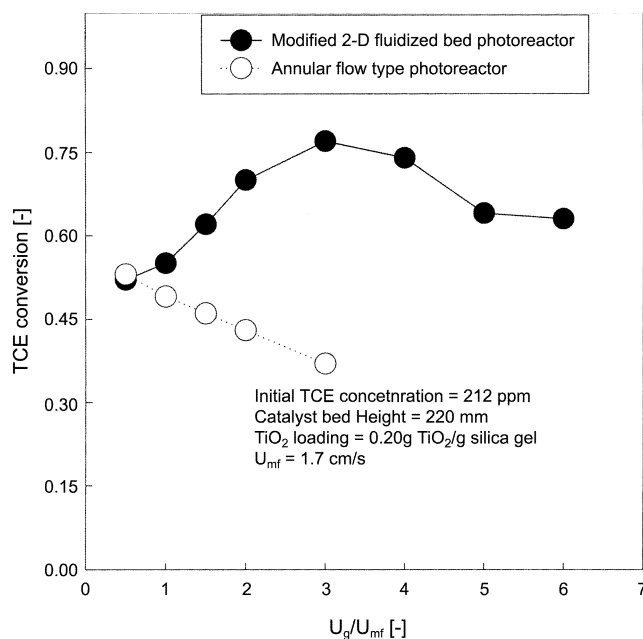Fig. 3. Effect of TiO₂/silica gel ratio on TCE conversion.

tion increases with increasing TiO_2/SiO_2 ratio >0.05 g due to the increase of photoreaction participation of TiO_2/SiO_2 photocatalyst. However, TCE conversion exhibits a maximum value at a ratio of $TiO_2/SiO_2=0.2$ at $U_g=3.0U_{mf}$. Thereafter, the degradation of TCE with a further increase in TiO_2/SiO_2 ratio could be resulting from the increment of unloaded TiO_2 on silica gel that may cause segregation between tiny TiO_2 powders (40-200 nm) and the unsupported silica gel, which causes poor fluidization such as slugging and channeling. Thus, the overloaded TiO_2 on silica gel exhibits a decrease of TCE conversion as in the case of photocatalytic ammonia synthesis in a fluidized bed reactor [Yue and Khan, 1983] of physically mixed iron-doped TiO_2 and γ-alumina. From these results, it can be claimed that good fluidization is essential to enhance the photocatalytic activity in an annulus fluidized bed and the amount of supporting TiO_2 on SiO_2 is an important factor to obtain good fluidization characteristics.

The effect of U_g on TCE conversion is shown in Fig. 4 where TCE conversion in the fluidized bed reactor is comparable with that in an annular flow type photoreactor at $U_g<1.0 U_{mf}$ since UV light only irradiates the front and rear sides of the reactor. Thus, contacting between UV light and TCE is very restricted and the UV light is unable to penetrate into interior of the photocatalyst bed. With increasing U_g above $1.3 U_{mf}$, TCE conversion in the photocatalytic degradation increases due to the increase of UV light transmission [Lim et al., 2000a]. However, TCE conversion exhibits a maximum value at $U_g=3.0 U_{mf}$ ($\varepsilon_g=0.72$). Thereafter, degradation of TCE with a further increase in U_g may be resulting from bypassing of TCE gas through bubbles and decrease of gas residence time in the reactor [Coates and Rice, 1974]. Yue and Khan [1983] reported that NH_3 production yield in a two dimensional flat-fluidized bed by photocatalysis exhibits a maximum value at $1.8 U_{mf}$ that is comparable to the result of this study. Therefore, photocatalysis of TCE degradation requires sufficient residence time in the reactor having a suitable TCE gas velocity to form proper bubble size for good contacting
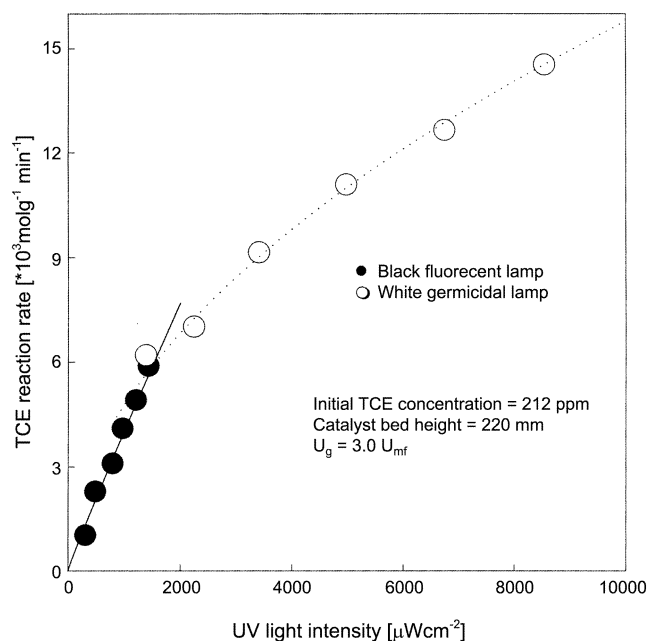
Fig. 5. Effect of UV light intensity on TCE conversion.

Fig. 6. Effect of wavelength of the UV light lamp on TCE conversion.

between UV light and TiO$_2$-TCE.

A photocatalytic reaction occurs in two regimes with respect to light intensity: the first-order regime where the electron-hole pairs are consumed more rapidly by chemical reactions than by recombination reaction that decrease the photocatalytic reaction rate and the half-order regime where the recombination rate is dominant one [Peral and Ollis, 1992].

The functional dependence of UV intensity on the photocatalytic reaction rate is shown in Fig. 5. At the illumination level appreciably above one sun equivalent (1-2 mW/cm^2), the reaction rate increases with the square root of the light intensity. When UV intensity is below one sun equivalent, the reaction rate increases linearly with the light intensity. As can be seen in the figure, the reaction rate dependency on the UV intensity follows a power law [Ollis et al., 1991].

$$R=R_oI^N \qquad (1)$$

The exponent values of the black and white lamps are found to be 0.48 and 0.98, respectively, as found previously [Peral and Ollis, 1992; Ollis et al., 1991].

The effect of wavelength of the UV light on TCE conversion is shown in Fig. 6. As can be seen, the germicidal white lamp (254 nm) shows higher TCE conversion than the fluorescent black lamp (365 nm). Both lamps have sufficient energy to promote electrons from the valence band to the conduction band of TiO$_2$. However, the higher output of photon flux with the germicidal lamp should lead to higher TCE conversion since photon fluxes of the germicidal lamp are higher than those with the black light lamp [Kim and Hong, 2002]. In addition, it has been reported that shorter wavelength light is adsorbed more strongly by TiO$_2$ particles than the longer one. Therefore, the penetration distance of photons into TiO$_2$ particles is shorter and electrons and holes are formed closer to surface of the particles. Then, they take less time to migrate onto the particle surface and hence have less time to participate in energy
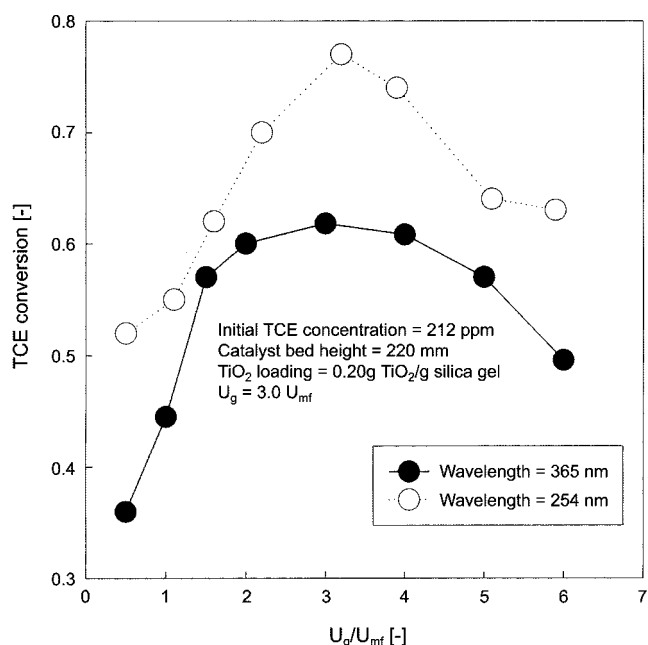
wasting recombination reactions before useful surface (or near-surface) reactions take place [Matthews et al., 1992]. Thus, the shorter wavelength of 245 nm irradiation is more effective in promoting photodegradation of TCE than the longer wavelength (365 nm) irradiation.

The effect of O$_2$ concentration on TCE conversion with variation of U$_g$ is shown in Fig. 7. As can be seen, TCE conversion in-
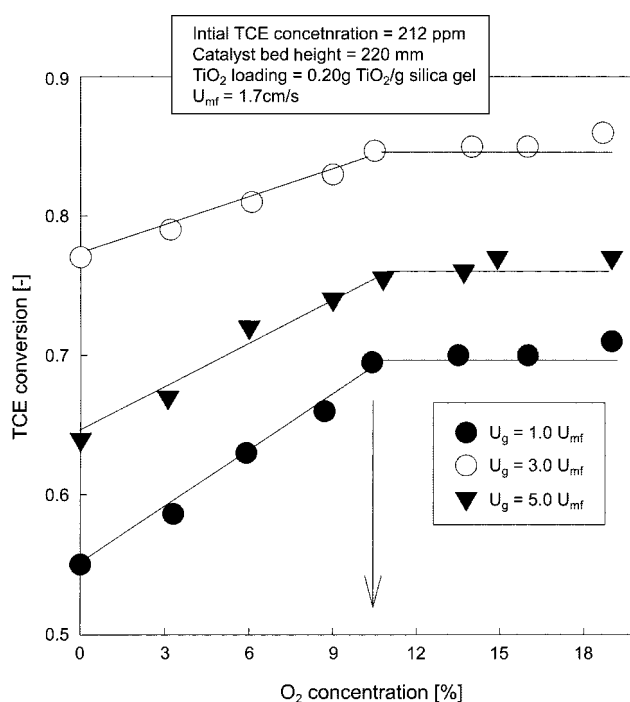

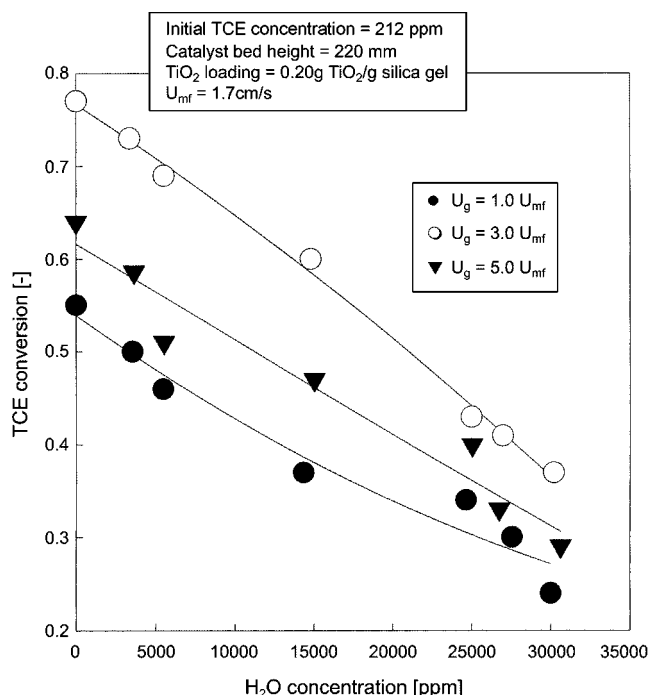**Fig. 7. Effect of O$_2$ concentration on TCE conversion with a variation of U$_g$.**

Fig. 8. Effect of H_2O concentration on TCE conversion with a variation of U_g.

creases with O_2 concentration up to 10% and remains constant with a further increase in O_2 concentration. Oxygen plays as electron acceptor in the whole electron-hole generation process. As TiO_2 is photocatalytically excited to generate electron-hole pairs, O_2 adsorbs on the surface of TiO_2 and reacts with electrons to form O^{2-} that decrease opportunity of the recombination process of electron-hole generation by the photocatalytic reaction [Wang et al., 1998]. Thus, TCE conversion increases with O_2 concentration up to 10%. From this experimental result, it may be noticed that the optimum condition of O_2 concentration is approximately 10% based on the maximum TCE conversion in the annulus fluidized bed photoreactor.

The effect of H_2O concentration on the TCE conversion with a variation of U_g is shown in Fig. 8 where TCE conversion decreases with H_2O concentration at the given $U_g=1.0, 3.0, 5.0\ U_{mf}$. The decrease of TCE conversion with H_2O can be attributed to the hydroxyl group from hydrolysis of TiO_2 that can combine with TCE by hydrogen bonding or covalent bond formation. It can also form hydrogen bonding with water molecules, creating a competition for adsorption between TCE and water molecules. In addition, moisture accumulation on the surface of TiO_2 may mask the active sites of adsorption to prevent adsorption of TCE [Wang et al., 1998]. Therefore, it can be claimed that TCE conversion decreases with increasing H_2O concentration with a variation of U_g in the annulus fluidized bed photoreactor.

CONCLUSIONS

The photocatalytic degradation characteristics of TCE (Trichloroethylene) have been determined in an annulus fluidized bed photoreactor over TiO_2/SiO_2 catalyst. The optimum condition of U_g based on the maximum TCE conversion is found to be 3.0 U_{mf} (5.1 cm/

s). The degradation efficiency of TCE increases with light intensity but decreases with wavelength of the UV lights and H_2O concentration in the fluidized bed of TiO_2/silica-gel catalyst. The optimum concentration of O_2 for TCE degradation is found to be approximately 10%.

NOMENCLATURE

C_{O2}	: concentration of O_2 in gas phase [ppm]
C_{H2O}	: concentration of H_2O in gas phase [ppm]
C_{TCE}	: concentration of TCE in gas phase [ppm]
H	: catalyst bed height [mm]
I	: UV light intensity [$\mu W\ cm^{-2}$]
R	: TCE photoreaction rate [$molg^{-1}min^{-1}$]
T	: reaction temperature [K]
W	: mass of TiO_2 photocatalyst [g]
U_{mf}	: minimum fluidization gas velocity [$cm\ s^{-1}$]
U_g	: superficial gas velocity [$cm\ s^{-1}$]
X	: fractional conversion of TCE [-]
ε	: voidage of the catalyst bed [-]

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