Effects of Water Vapor, Molecular Oxygen and Temperature on the Photocatalytic Degradation of Gas-Phase VOCs using TiO₂ Photocatalyst: TCE and Acetone

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Abstract

Recent development of photocatalytic degradation method that is mediated by TiO₂ is of interest in the treatment of volatile organic compounds (VOCs). In this study, trichloroethylene (TCE) and acetone were closely examined in a batch scale of photo-reactor as a function of water vapor, oxygen, and temperature. Water vapor inhibited the photocatalytic degradation of acetone, while there was an optimum concentration in TCE. A lower efficiency was found in nitrogen atmosphere than air, and the effect of oxygen on photocatalytic degradation of acetone was greater than on that of TCE. The optimum reaction temperature on photocatalytic degradation was about 45°C for both compounds. No organic byproducts were detected for both compounds under the present experimental conditions. It was ascertained that the photocatalytic reaction in a batch scale of photo-reactor was very effective in removing VOCs such as TCE and acetone in the gaseous phase.

1. INTRODUCTION

Many classes of VOCs such as halogenated hydrocarbons, ketones, alcohols and aromatic compounds have been widely used in many industries, and often found in the emission flow (Shen *et al.*, 1993). These extensive uses have led to water and air pollution, particularly indoor work-place air pollution (EPA, 1987). Many VOCs are known to be toxic and considered to be carcinogenic. The most significant problem related to the emission of VOCs is the potential production of photochemical oxides; for example, ozone and peroxyacetyl nitrate (PAN).

The TiO₂-sensitized photodegradation of organic compounds has been proposed as an alternative Advanced Oxidation Process (AOP) for the decontamination of water and air. The process is initiated from the

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generation of hole-electron pairs on the semiconductor upon absorbing the ultra-violet (UV) light with energy being equal or higher than the band gap energy. Electrons and holes are photo-generated in the bulk of the semiconductor, and move to the particle surface; electrons reduce an electron acceptor such as molecular oxygen and holes can oxidize electron donors including adsorbed water or hydroxide anion to give hydroxyl radicals.

Recently, some researchers have examined the degradation of TCE through the gas phase photocatalytic reaction. In order to determine the kinetics of conversion of trace (0~100 ppm) TCE, Dibble and Raupp (1992) systematically investigated the photo-oxidation in air using both a fixed-bed reactor and a fluidized bed reactor. They showed that trace water vapor was essential to maintain the photocatalytic activity of the catalyst for an extended period, but higher water vapor levels were strongly inhibitory. Anderson *et al.* (1993) studied the dependency of the TCE photocatalytic degradation rate based on the light intensity, feed composition (TCE, O_2, H_2O) and temperature in a bed reactor packed with TiO_2 pellets. They showed that the reaction occurred in a first order reaction with respect to the light intensity, and it was independent of the concentration in the range of 37~450 ppm, 0.01~0.2 of oxygen mole fraction and 0.001~0.028 of water vapor mole fraction. Reaction temperature did not affect the reaction rate in the range of 23 to 62°C.

Heterogeneous photocatalytic oxidation of acetone using TiO_2 follows another degradation process. Peral and Ollis reported that the water vapor inhibited the oxidation of acetone (Peral and Ollis, 1992). On the contrary, some researchers showed the water vapor could enhance the photocatalytic oxidation of hydrocarbons such as formic acid (Muggli and Falconer, 1999).

The purpose of this work is to find the optimum condition in the photocatalytic degradation of VOCs including TCE and acetone as a function of water vapor, oxygen, and temperature. A batch scale of photo-reactor was applied prior to the acquisition of fundamental data from a scaled-up photo-reactor and the applica-

tion of continuous process for the gas-solid heterogeneous photocatalytic reaction.

2. MATERIALS AND METHODS

2. 1 Materials and reactor system

All of the chemicals used in this work were reagent-grade. The liquid phase VOCs were products of Aldrich (trichloroethylene (TCE)-anhydrous, 99%, acetone-A.C.S. reagent, 99.5%). Photocatalyst was prepared with TiO_2 solution (STS-01, anatase, 7 nm in diameter, 300 m^2/g for specific surface area, Ishihara Sangyo Co., Japan), tetraethyl orthosilicate (TEOS, 98%, Aldrich, U.S.A.), dimethoxy dimethyl silane (DMDMS, 95%, Aldrich, U.S.A.), isopropyl alcohol (IPA, anhydrous, 99.5%, Aldrich, U.S.A.) and nitric acid (65 wt% solution in water, Aldrich, U.S.A.). Deionized and double distilled water was used to generate the water vapor and to prepare the photocatalyst.

A batch scale of photo-reactor made of Pyrex glass depicted schematically in Fig. 1 had a 100 mm inside diameter, 210 mm height and 1,600 cm^3 total volume. The upper part of the reactor was sealed with a Teflon lid. A vertical UV lamp (outside diameter of 15.5 mm, length of 210.5 mm) was centered of the reactor. Pyrex glass tube coated by the photocatalyst (TiO_2) at the internal surface was fixed at the outside of UV lamp resulting in 3 mm gap. The effective dispersion was achieved by a magnetic stirrer. The concentration of VOCs could be measured by a gas chromatograph (Model HP 6890, Hewlett-Packard, U.S.A.) equipped with a HP-5 capillary column (30 m length, 0.25 μm film thickness and 0.32 mm internal diameter) and a flame ionization detector.

The light source was the germicidal lamp (Model G6T5, 6 W, Sankyo Denki Co., LTD, Japan) and fluorescent black light lamp (Model F6T5 BL, 6 W, Sankyo Denki Co., LTD, Japan). The wavelength of the germicidal lamp ranged from 200 to 300 nm with the maximum light intensity at 254 nm, and that of the black light lamp ranged from 300 to 400 nm with the
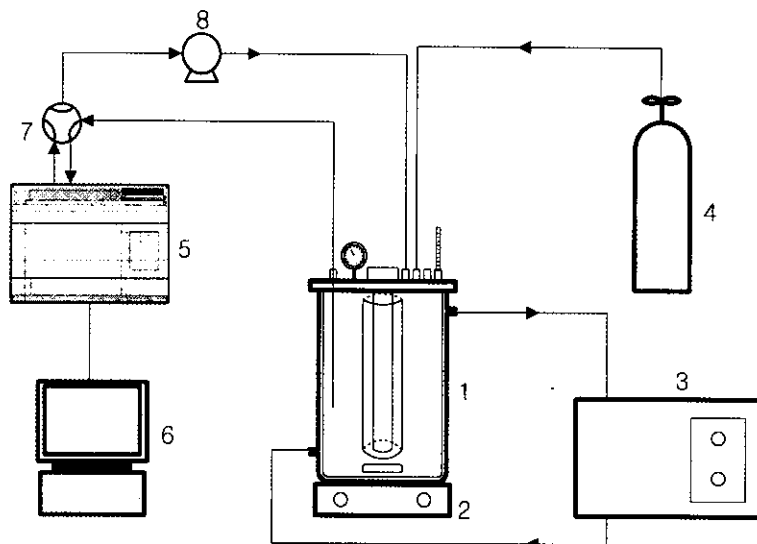
1. Photo batch reactor   2. Magnetic stirrer   3. Thermo–bath & circulator   4. Gas cylinder (air or N_2)
5. Gas Chromatograph   6. Data acquisition system   7. Six–port GC valve system   8. Gas pump

Fig. 1. Schematic diagram of the experimental apparatus.

maximum light intensity at 352 nm.

2. 2 Preparation of photocatalyst

Photocatalyst solution was prepared through a three –step process as follows: TEOS (2 g) and DMDMS (1 g) were added to the IPA (10 g) on a vessel connected to a condenser at room temperature (1st step). A solution combined with IPA (10 g), deionized water (0.5 g) and nitric acid (0.03 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 (35 g) was dropped in the solution combined with IPA (15 g), deionized water (15 g) and the solution (22.5 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_2 thin film photocatalyst was formed by the dip–coating method. After filling a Pyrex glass tube with the TiO_2 photocatalyst solution, it was removed from the Pyrex glass tube at a constant rate of 5 mm/ min. Then, the Pyrex glass tube coated with TiO_2 was dried at 120°C for one hour.

2. 3 Experimental method

The batch reactor was flushed and filled with dry air prior to the injection of liquid phase VOCs and water. The desired amount of water was then injected and allowed to evaporate, mix, and reach adsorption equilibrium with the TiO_2 thin film photocatalyst. Next, the desired amount of VOCs was injected in the liquid phase and allowed to evaporate, mix, and reach gas–solid adsorption equilibrium. The concentration of VOCs was monitored with reaction time using an automated sampling system. Right after the concentration of VOCs was stabilized, the UV lamp was turned on and the concentration of VOCs was recorded with the reaction time throughout the test.

Sampled VOC were circulated by a low–flow diaphragm pump (Model SP 600 EC–LC, SP J. Schwarzer GmbH u. Co., Germany). Analysis was made by a gas chromatograph with pure helium as a carrier gas. Temperatures of the injector and column were maintained at 120 and 200°C, respectively. The flame ionization detector attached in gas chromatograph was maintained at 250°C.

3. RESULTS AND DISCUSSION

3. 1 Characterization of catalyst

Uniform and semi-transparent TiO_2 thin film with a thickness of about 65 nm was formed on a Pyrex glass tube substrate. The coating condition was observed through scanning electron microscopy (SEM, Philip SEM-535M). Fig. 2 shows well-dispersed particles. The film consists of small crystalline particles with an average diameter of about 40 nm. Since the average particle size in the in the TiO_2 solution was about 7 nm, it is assumed that the particles aggregated during heat treatment. The used TiO_2 was found to be Anatase by
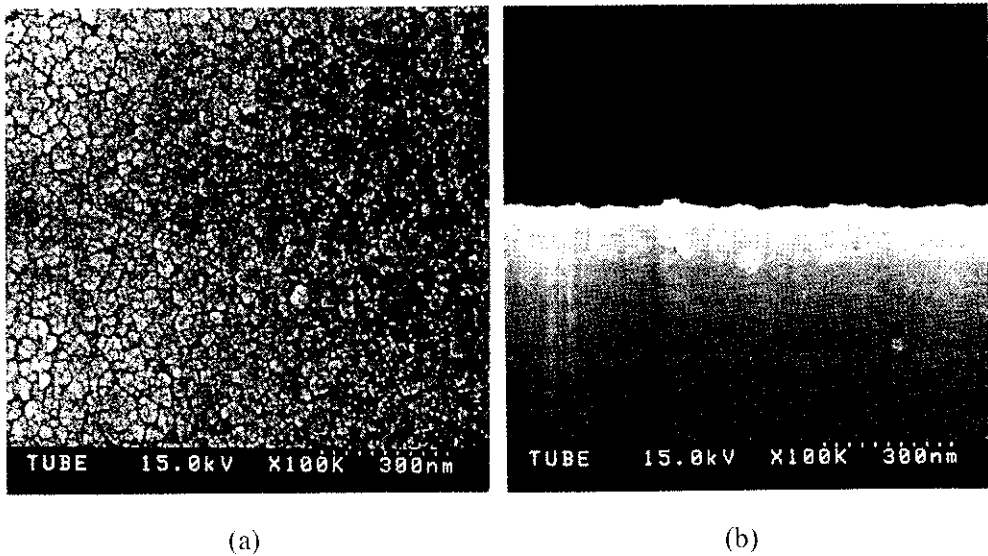

(a)   (b)

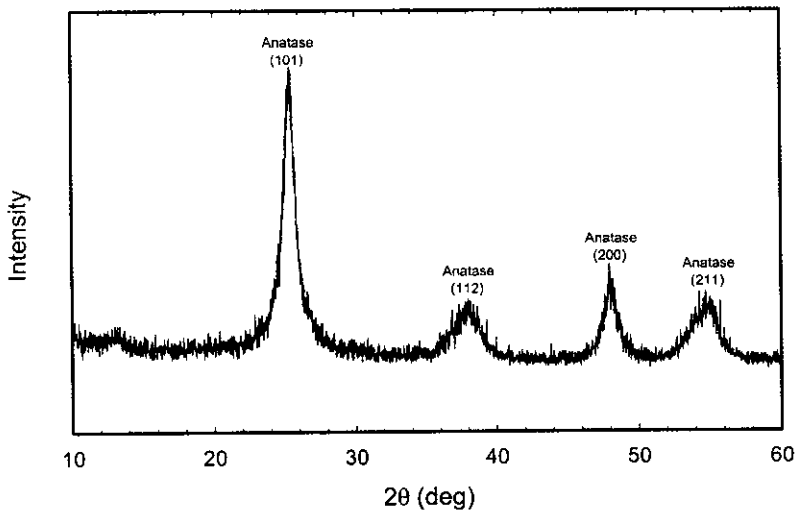Fig. 2. SEM photographs of (a) top and (b) cross-sectional views of the TiO film on the Pyrex glass tube.

Fig. 3. X-ray diffraction patterns of TiO_2 film.

means of X-ray diffraction (Rigaku D/MAX-III (3 kW) diffractometer). Fig. 3 shows the XRD patterns for TiO₂. Four remarkable peaks were observed at the angles of 2θ: 25.38, 38.14, 48.04 and 55.02. No other clear peaks were observed except the four peaks attributed to anatase (Sanjinés et al., 1994).

Specific surface area of the prepared TiO₂ particles was determined by BET method, instrumented Micrometritics ASAP 2,100 at 77.5 K. The BET surface area of the prepared TiO₂ particles was 277 m²/g.

3. 2 Effect of water vapor

Numerous studies revealed a dual function of water vapor. The influence of water vapor in gas phase photocatalytic degradation depends on the species of contaminants. Some reports presented that the water vapor should strongly inhibit the oxidation of isopropanol, TCE, and acetone; while it enhances toluene oxidation, and gives no significant effect on 1-butanol (d'Hennezel et al., 1998; Wang et al., 1998; Alberici and Jardim, 1997; Luo and Ollis, 1996).

In order to examine the effect of water vapor, different volume fraction of water vapor was added to a fixed VOCs concentration. Firstly, water vapor varied from 0 to 4.0 vol.% in a fixed TCE concentration of 315 ppm. As reported in the published literatures, photocatalytic degradation of TCE was very rapid due to chlorine radicals, leading to the chain reaction and

subsequently resulting in an unusual high quantum yield (Alberici and Jardim, 1997; d'Hennezel and Ollis, 1997; Luo and Ollis, 1996). The present study confirmed its high photocatalytic conversion of nearly 100%. Fig. 4 (a) shows the photocatalytic conversion of TCE versus the irradiation time at various water vapor concentrations. TCE conversion was enhanced by water vapor up to 1.0 vol.% corresponding to about 13.5% of relative humidity, and then began to inhibit it above 1.0 vol.%. In the presence of water vapor, the hydroxyl radicals formed on the illuminated TiO₂ can not only directly attack VOC molecules but also suppress the electron-hole recombination (Fox and Dulay, 1993; Mark et al., 1993). Hydroxyl group or water molecules behave as a hole trap, forming surface adsorbed hydroxyl radicals. However, under higher humidity conditions, the water molecules could compete with the TCE molecules on the catalyst surface sites during the adsorption (d'Hennezel et al., 1998; Wang et al., 1998; Luo and Ollis, 1996). Therefore, TCE conversion decreased with increasing humidity.

The effect of concentration of water vapor for a given acetone concentration was also examined. Fig. 4 (b) indicates that the addition of water vapor decreases the conversion of acetone. Although water molecules could form hydroxyl radicals behaving as a simultaneous hole trapper, water vapor seemed to hinder the adsorption of acetone molecules on the catalyst surface
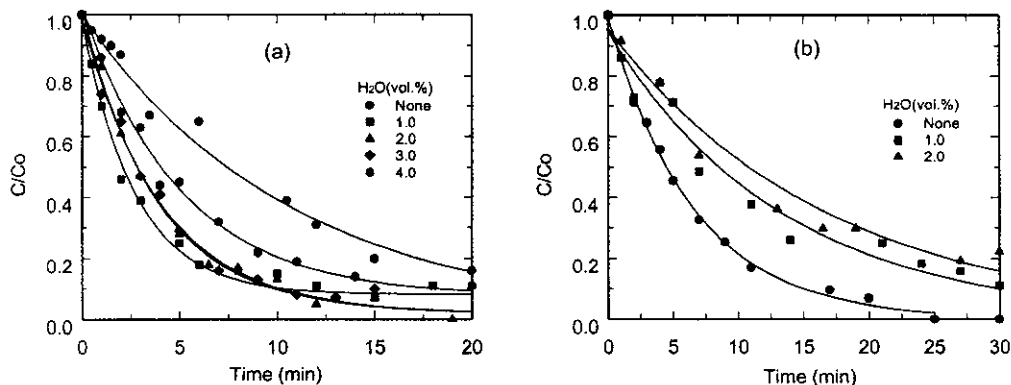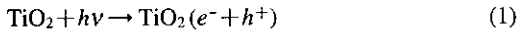

Fig. 4. Photocatalytic conversion of TCE and acetone according to quantity of water vapor ((a) TCE (Co = 315 ppm), (b) acetone (315 ppm); Temp.: 45°C).

(Vorontsov et al., 1999; Sauer and Ollis, 1994).

3. 3 Effect of oxygen

When the TiO_2 particles are illuminated by photons with appropriate energy, the valence band electrons of the TiO_2 can be excited to the conduction band, creating highly reactive electron (e^-) and hole (h^+) pairs (reaction (1)). Those migrate to the TiO_2 solid surface and are trapped at different sites. Those electrons and holes play a part in the reduction and oxidation of photocatalytic reaction, respectively. The photo-generated holes may be trapped by hydroxyl ions on the surface forming hydroxyl radicals (reaction (2)) (Miller and Fox, 1993; Munuera et al., 1979), and the electrons may be trapped by an electron acceptor of oxygen forming oxygen species $(O_2^- \cdot$; super oxide radical) on the surface (reaction (3)).

$$TiO_2 + h\nu \rightarrow TiO_2 (e^- + h^+) \qquad (1)$$

$$h^+ + OH^- \rightarrow OH \cdot \qquad (2)$$

$$O_2 + e^- \rightarrow O_2^- \cdot \qquad (3)$$

If water vapor takes part in the gas-solid photocatalysis, the super oxide radicals will be involved in the reaction with water molecules, eventually forming the hydroxyl radicals as shown in reaction (4). Thus, the photocatalytic degradation of VOCs can be increased due to the formation of hydroxyl radicals (Fox et al.,

1990).

$$2O_2^- \cdot + 2H_2O \rightarrow 2OH \cdot + OH^- + O_2 \qquad (4)$$
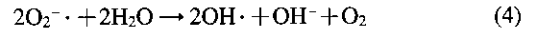
In order to examine the effect of oxygen on the photocatalytic conversion of TCE and acetone, the photocatalytic degradation tests were carried out at the atmosphere of synthetic air (20.9% O_2) and pure nitrogen with O_2-free. Fig. 5 shows the oxygen dependency on the photocatalytic conversion of TCE and acetone. It informs that the oxygen facilitates the photocatalytic conversion of acetone. As previously stated, while oxygen as an electron acceptor forms hydroxyl radicals, nitrogen has nothing to do with the formation of hydroxyl radicals. For TCE, however, the presence of oxygen has no effect on the photocatalytic conversion as shown in Fig. 5(a). Several researchers reported that TCE photocatalytic degradation was predominantly through a chain reaction by chlorine radicals (Luo and Ollis, 1996). In this study, it seems that chlorine radicals as well as hydroxyl radicals are formed through the photocatalytic reaction of TCE. Thus, oxygen may not affect the photocatalytic conversion of TCE.

3. 4 Effect of temperature

As a whole, temperature is one of the most important factors in gas-solid heterogeneous reactions. However, photocatalytic reactions are not sensitive to minor variation in temperature (Fox and Dulay, 1993).
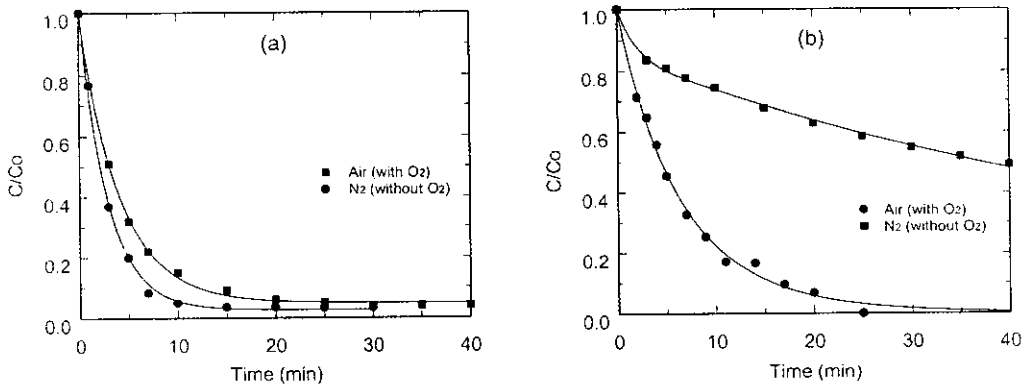

Fig. 5. Photocatalytic conversion of TCE and acetone at the presence and absence of oxygen ((a) TCE (Co = 315 ppm, water vapor = 1.0 vol.%), (b) acetone (315 ppm, water vapor = 0.0%); Temp.: 45°C).

From the study of Pitchat and Hermann (1989) for de-hydrogenation of alcohol over Pt/TiO2, it was found that the desorption step of hydrogen was rate determining at lower temperature. On the contrary, the photocatalytic reaction rate decreased over 70°C. In this case, adsorption should be the rate determining step (Pitchat and Hermann, 1989).

Fig. 6 shows the relative output from the 254 nm UV lamp at various temperatures. It showed that the light intensity had a maximum output at 42.5°C. The effect of reaction temperature on the photocatalytic conversion of TCE and acetone was investigated at three different temperatures (25, 45 and 75°C). Fig. 7 demonstrates the temperature dependency on the photocatalytic conversion. The most efficient temperature was about 45°C. At lower temperatures, desorption of the products from the photocatalyst surface was the rate determining step, whereas at higher temperatures the adsorption of the reactants dominated the reaction rate.

4. CONCLUSIONS

Photocatalytic reactivity of VOCs such as gaseous TCE and acetone, as a preliminary study prior to the continuous process including gas–solid heterogenous reaction, was investigated in a batch scale of photo-reactor as a function of water vapor, oxygen, and temperature. The influence of water vapor depends on the species of contaminants. Water vapor inhibited the photocatalytic degradation efficiency of acetone, while there was an optimum concentration in TCE. For the effect of oxygen on the photocatalytic conversion of TCE and acetone, oxygen is an essential component in photocatalytic reactions because it traps photo–generated electrons on semiconductor surfaces and decreases recombination of electrons and holes, but the effect of oxygen on photocatalytic degradation of acetone was greater than that of TCE. As for the effect of temperature on the photocatalytic conversion of TCE
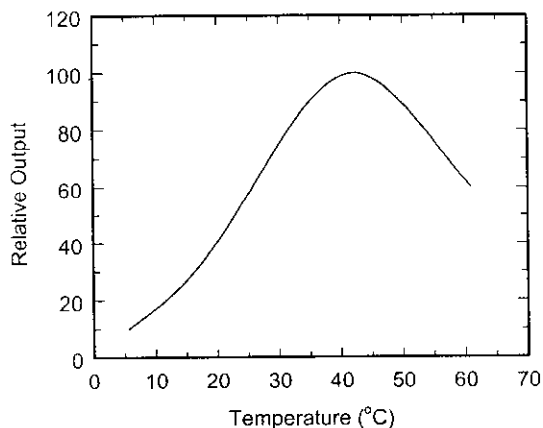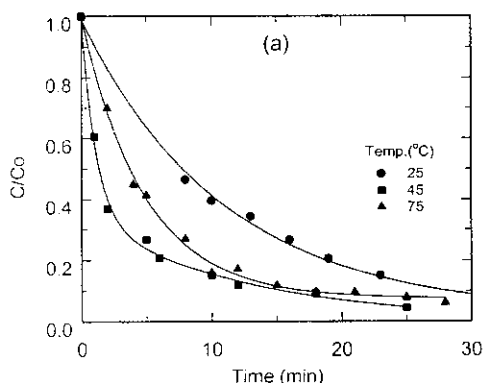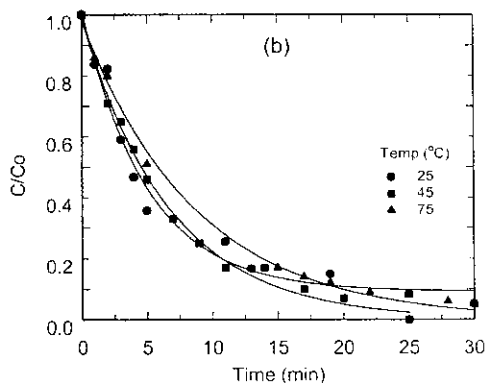
Fig. 6. Relative output germicidal UV lamp according to various bulb wall temperature at 254 nanometers (presented by Atlantic Ultraviolet Corporation).

Fig. 7. Photocatalytic conversion of TCE and acetone according to temperature of reactor ((a) TCE (Co = 315 ppm, water vapor = 1.0 vol.%), (b) acetone (315 ppm, water vapor = 0.0%)).

and acetone, the optimum reaction temperature on photocatalytic degradation was about 45°C.

In conclusion, it was confirmed in this study that the photocatalytic reaction using a batch scale of photoreactor was very effective in removing VOCs such as TCE and acetone in the gaseous phase. Further work, however, must be followed to ensure the practical treatment of VOCs.

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