

Removal of Volatile Organic Compounds by Photo-Catalytic Oxidation

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Abstract

Volatile Organic Compounds (VOCs) are considered as the precursors of atmospheric ozone and photochemical smog formation. In particular, chemical plants have produced a lot of VOCs and thus they have been forced to reduce or remove air emissions from the on-site chemical facilities. For the effective removal of VOCs produced in the chemical plants, the authors employed a titanium oxide (TiO₂) mediated photo-catalytic oxidation method. The initiation methods employed in this study to produce oxygen radicals for the photo-catalytic oxidation of the VOCs were Ultra-Violet (UV), Non-Thermal Plasma (NTP), and a combination of UV and NTP. This study focused on a comparison of the removal efficiencies of VOCs as a function of the initiation method such as NTP and/or UV techniques. Removal efficiency change of VOCs was investigated as a function of the wavelength of the UV lamp (254, 302, and 365 nm) and the degree of TiO₂ coating (10 and 30%). In this study, it was identified that removal efficiencies of the VOCs under the normal air environment were much better than those under the nitrogen gas environment containing small amount of oxygen. Removal efficiency by NTP technique was much better than the UV or the combination of UV and NTP techniques. In a comparison of UV wavelengths employed, it was found that shorter wavelength showed better removal efficiency, compared with longer ones. When the removal efficiencies of VOCs were compared in terms of the degree of TiO₂ coating, the higher TiO₂ coating showed better removal efficiency than the lower TiO₂ coating.

1. INTRODUCTION

Automobile, printing, painting, storing and pumping of gasoline, and oil refinery and chemical processes are the major emission sources of Volatile Organic Compounds (VOCs) (Lee and Cho, 1999; Chun *et al.*, 1998). VOCs could be the precursors for the formation of the ground level ozone and of photochemical smog. In particular, since some of VOCs (such as benzene and chloroform) can be potential carcinogen compounds, they have been regulated as hazardous air pollutants or air toxics by the Clean Air Act Amendments

(CAAA) of 1990 (US EPA, 1992; Lee, 1991; DPC, 1990). Thus it is very important to effectively remove VOCs from the emission sources. Numerous VOC removal technologies including reuse or recycle, incineration, absorption, adsorption, and biological treatment such as biofiltering and bioscrubbing have been developed (Cha *et al.*, 2000; Roark *et al.*, 2000; Wander, 2000; Chun *et al.*, 1998; Buonicore, 1992). However, these removal technologies often produce secondary pollutants or hazardous by-products. Thus new removal technologies which do not cause secondary pollution have been developed. Disposal or removal technology by a non-thermal plasma is one of the developing new technologies. Non-thermal plasma tech-

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nology is employing as a removal method which uses electro-physicochemical processes, including radiation, oxidation, and decomposition, of air pollutants such as SO_x, NO_x, and VOCs (Person and Ham, 1998; Clements *et al.*, 1992; Masuda and Nakao, 1985). The basic principle of a non-thermal plasma technique is to generate plasma by a corona discharge, produce ionic species of the air molecules in the discharge space by electrolytic dissociation, and remove pollutants by impacts with active radicals produced by the ionic species. Since removal of air pollutants by a non-thermal plasma technique generally does not cause the secondary pollution, air cleaning technologies by non-thermal plasma method have been widely used as the control methods of automobile exhaust gases and indoor air pollution (Lee, 1997).

The previous studies, which used a non-thermal plasma technique, mainly focused on removal of single or simplified air pollutants with high concentrations ranged between hundreds and thousands of ppm (Hung, 2000; Park, 1998; Lee, 1997). However, in fact, most of the chemical plants are simultaneously producing a lot of chemicals. In addition, even though several removal studies of VOCs by a non-thermal plasma technique have been performed, there are lots of problems which have not been solved. Especially, a comparison study on removal efficiencies of the VOCs in photo-catalytic reactions by UV and/or plasma methods is not common (Kamat, 1993). From these points of view, this study is to compare the removal efficiencies of VOCs, which have been produced as high concentrations from chemical plants or complex, through the TiO₂ mediated photo-catalytic reaction initiated by the non-thermal plasma and/or UV irradiation.

2. MATERIALS AND METHODS

Figure 1 shows the schematic diagram of the photo-catalytic reaction employed in this study. The photo-catalytic reactor had a dimension of 0.47 × 0.35 × 0.2 m (0.033 m³ volume) and it was made of acryl resin. The reaction system consisted of a plasma generator, alu-

minum mesh coated with TiO₂, a ultraviolet (UV) lamp, a fan for effective mixing of compounds in the reactor, a heater to make vapor of liquid chemicals, and an air sampling system composed of an air sampling pump and a tedlar bag. The TiO₂ mediated non-thermal plasma generator shown in Figure 1 was made of discharge lines, guards for protection of the discharge line, ground electrode, and aluminum wire-plate (400 × 300 mm) coated with a TiO₂ (Degussa P-25).

The VOCs investigated in this photo-catalytic reactions were a mixture of 9 VOCs which have been emitted with high concentrations from chemical plants or petrochemical complex. The VOC mixture was composed of acetaldehyde, acetone, methylethylketone, n-hexane, benzene, toluene, xylene, chloroform, and dichloromethane.

10 µg of the liquid sample was taken by a micro syringe from each chemical bottle which contains high purity chemicals and the liquid chemicals taken were injected into the small suction flask. The liquid mixture in the flask was vaporized by a mini-heater. All the vaporized VOCs were introduced into the reaction system at room temperature by the reduced pressure generated by a pump attached in the air sampling system. The reaction system was keeping inert conditions by a high purity nitrogen purging before the vaporized VOCs were entered into the reaction system. After the sample introduction into the reactor was complete and the introduction part was closed. And the entire reaction system was tightly sealed. The VOCs introduced into the reactor were homogeneously mixed-up for 5 minutes by a fan located in the reactor. After the sampling system was open, the reaction initial samples were taken for a minute with a flow rate of 4 L/min by an air sampling pump and tedlar air sampling bag before the photo-catalytic reaction starts. The photo-catalytic reaction started after turning on the plasma generating system and/or the UV lamp. After the photo-catalytic reaction (for 30 minutes) was completed, the reacted samples were taken with the same sampling methods and conditions as the reaction initial samples. The removal efficiencies of the VOCs were investigat-

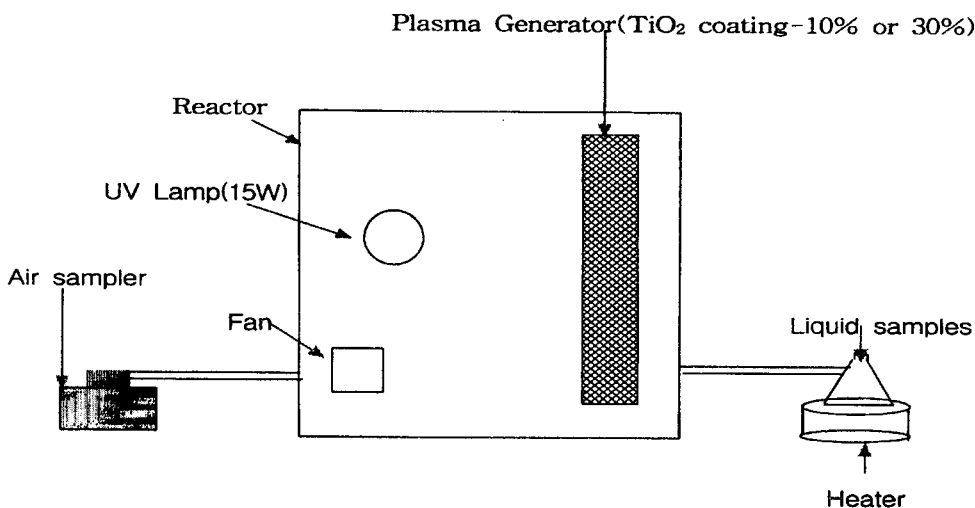


Fig. 1. A schematic diagram of the photo-catalytic reaction.

ed as a function of the following variables: a residence time in the photo-catalytic reactor, a carrier gas composition (air or nitrogen), a degree of TiO_2 (Anatase type) coating (30% or 10%), a UV strength (254, 302, and 365 nm: the cut-off wavelength of the UV lamp with 15 W), and a combination of UV and plasma techniques. Three sets of experiment including reaction, sampling, and analysis of each photo-catalytic reaction to study were performed with the batch system. The components and concentrations of the samples taken from the reactor were analyzed by a GC-MSD (HP 5890 GC Series II and 5971 MSD with a Blank Detection Limit, 0.1 ppb) using a cryogenic concentration system (Donam System Inc.).

3. RESULTS AND DISCUSSION

3.1 Residence time

Figure 2 shows the average removal efficiencies (of the VOCs) as a function of residence time of the VOCs in the photo-catalytic reactor using TiO_2 (30% coating) and plasma initiation. About 45% of the VOCs were removed in 5 minutes of the photo-catalytic reactions. The removal efficiency of the VOC mixture became as about 73% and 85% as 30 minutes and 60

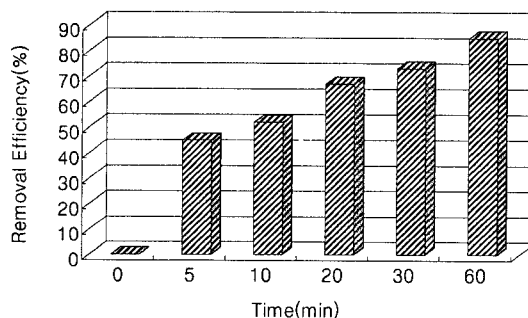


Fig. 2. Average removal efficiencies of the VOCs as a function of residence time.

minutes, respectively. The removal rates of the VOCs rapidly increased during the first 5 minutes after the reaction started, but the VOCs were not removed as much as within the reaction period of 5 minutes. Even though the removal efficiencies were slowly improved with increase of reaction or residence time, side reactions or effects by ozone produced from the plasma generator and/or the UV lamp also can increase. In addition, the removal rate of some VOC (such as chloroform) under certain conditions was very low up to the reaction period of 30 minutes. From these points of view, it was assumed that the reaction period of about 30 minutes could be proper for an easy comparison of

removal efficiencies of the VOCs in this study.

3.2 Carrier gas

In the photo-catalytic reactions by TiO₂ (30% coating) using non-thermal plasma, the removal efficiencies of the chloroform, dichloromethane, and hexane as a function of a carrier gas composition were shown in Figure 3. That is, this figure represents the removal effect of the specific three VOCs of a carrier gas change and a compositional element (chlorine content) change within VOC molecule in the photo-catalytic reactions.

The removal efficiencies under the normal air environment (21% oxygen + 78% nitrogen) were much greater than those under the nitrogen gas environment containing only small amount of oxygen. This represents that VOCs are removed by reacting with radicals containing oxygen rather than other nitrogen radicals. Under the nitrogen gas environment the removal efficiencies of chlorine compounds such as chloroform and dichloromethane were much lower than aliphatic hydrocarbon such as hexane.

In particular, only a very small amount of chloroform was removed due to a shortage of oxygen gas. This result suggests that the higher content of chlorine within the chemical structure of the VOC molecules in the TiO₂ mediated photo-catalytic reaction initiated by the non-thermal plasma, the lower removal efficiencies of the VOCs might be expected, in particular, under

the nitrogen carrier gas environment.

3.3 Degree of TiO₂ coating

In the photo-catalytic reactions using TiO₂ catalyst and non-thermal plasma, the average removal efficiencies of the VOCs as a function of a degree of TiO₂ coating were shown in Figure 4. The removal efficiency of the VOCs in the photo-catalytic reactions using the TiO₂ (30% coating) catalyst was about 73%, while that using TiO₂ (10% coating) catalyst was about 50%. The more amount of TiO₂ was coated on the aluminum wire-plate, the more TiO₂ surface could be used as the surface for the photo-catalytic reactions using by the TiO₂ photo-catalyst. This is because the more oxygen radicals in the photo-catalytic reactions with higher TiO₂ coating could be supplied for removal reactions of the VOCs. In a comparison of removal efficiencies of the VOCs in the TiO₂ mediated photo-catalytic reactions by the non-thermal plasma and the UV, the initiation method by the non-thermal plasma showed much better removal efficiencies than the initiation method by UV. This is because the non-thermal plasma could much more improve the removal efficiencies of the VOCs by the photo-catalytic reactions than the UV irradiation.

3.4 UV wavelength

Figure 5 shows the average removal efficiencies of

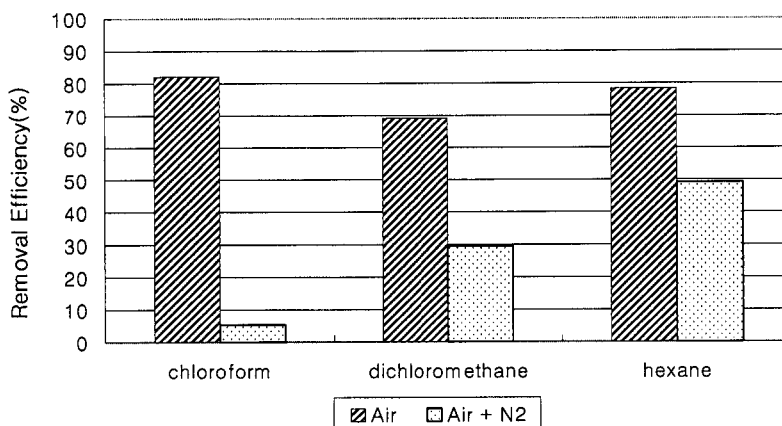


Fig. 3. The removal efficiencies of chloroform, dichloromethane, and hexane as a function of carrier gas composition.

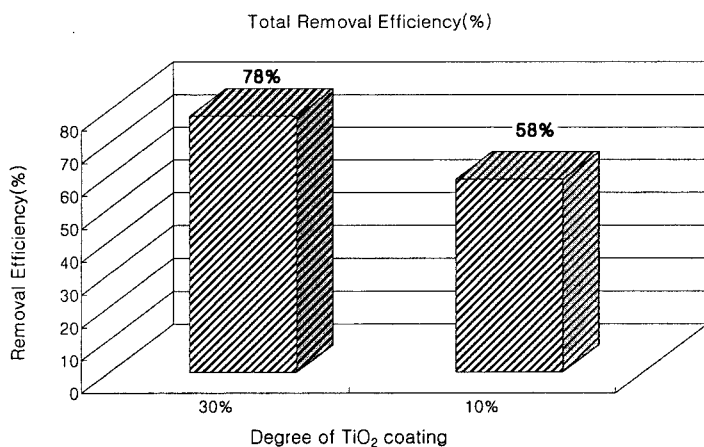


Fig. 4. Average removal efficiencies of the VOCs as a function of TiO₂ coating level in the photo-catalytic reactions using non-thermal plasma as an initiation method.

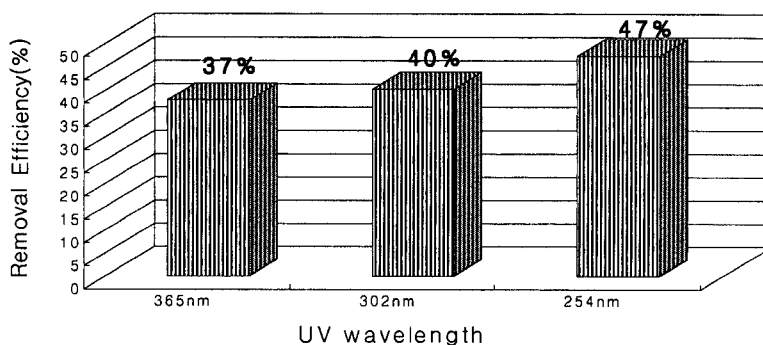


Fig. 5. Average removal efficiencies of the VOCs as a function of a UV wavelength using UV as an initiation method.

the VOCs as a function of UV wavelength in the TiO₂ (30% coating) mediated photo-catalytic reactions. The average removal efficiencies of the VOCs in the photo-catalytic reaction initiated by the UV lamp with 254 nm wavelength were relatively higher than those by the UV lamp with 302 nm and 365 nm wavelengths. This means that the shorter UV wavelength, the better removal efficiencies were observed. This is because the energy strength in the irradiation using the UV with shorter wavelength is greater than the UV with longer ones. That is, the more photon in the UV irradiation with shorter wavelength was produced, the more photon was used in the excitation for removal of the VOCs.

3.5 UV and plasma combination

In the TiO₂ (30% coating) mediated photo-catalytic reactions both using non-thermal plasma and UV techniques, better removal efficiencies of the VOCs were observed with shorter UV wavelength rather than longer wavelength (see Figure 6) likewise the reaction using the only the UV as an initiation method (see Figure 5).

Table 1 compares the removal effects of the VOCs based on an initiation method in TiO₂ (30% coating) mediated photo-catalytic reaction: In analysis of removal efficiency based on chemical structure of the tested VOCs, most of the VOCs represent the best removal effects in the photo-catalytic reactions initiated

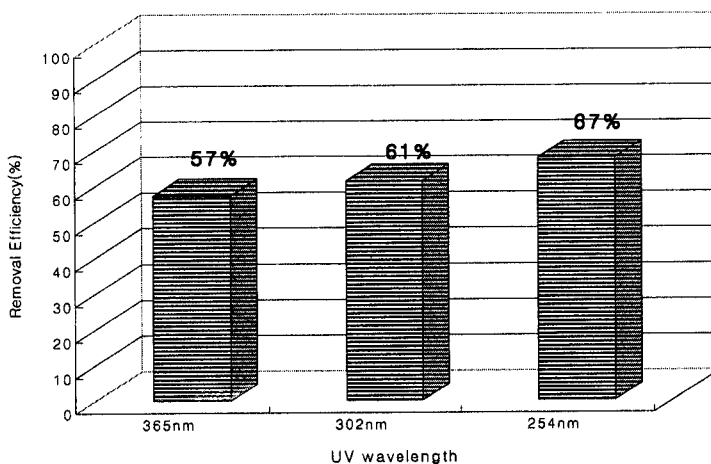


Fig. 6. Removal efficiencies of the VOCs as a function of UV wavelength in the photo-catalytic reactions with both UV and non-thermal plasma as an initiation method.

Table 1. A comparison of removal efficiency of the VOCs based on an initiation method in the TiO₂ (30% coating) mediated photo-catalytic reaction. (Unit : %)

| VOC | Initiation Method | | |
|--|-------------------|--------------------|--------------------------------|
| | UV (254 nm) | Non-thermal plasma | UV (254 m)+ Non-thermal plasma |
| Benzene | 34 | 66 | 55 |
| Toluene | 44 | 81 | 61 |
| Xylene | 57 | 100 | 94 |
| Aromatic VOC average removal | 45 | 82 | 70 |
| Hexane | 75 | 78 | 44 |
| Aliphatic VOC average removal | 75 | 78 | 44 |
| Acetaldehyde | 86 | 65 | 97 |
| Acetone | 65 | 82 | 86 |
| Methylethylketone (MEK) | 34 | 81 | 71 |
| Oxidized VOC average removal | 62 | 76 | 85 |
| Chloroform | 40 | 82 | 48 |
| Dichloromethane | 49 | 69 | 79 |
| Chlorinated VOC average removal | 45 | 76 | 64 |
| Total average removal | 54 | 78 | 71 |

by only the non-thermal plasma. However, the removal effects of the VOCs containing oxygen in their molecules, e.g., aldehyde and ketone, seem to represent the different results. That is, the removal effects of acetaldehyde and acetone in the initiation method combining the non-thermal plasma and the UV are better than those in initiation by only the non-thermal plasma. All the VOCs tested in the photo-catalytic reactions initiated by only the UV shows the worst re-

moval effects among three initiation methods tried.

Table 2 summarizes the average removal efficiencies of the VOCs in the TiO₂ mediated photo-catalytic reactions which employed the non-thermal plasma technique with a change of UV wavelength and a change of a degree of TiO₂ coating. Also, Table 2 shows the removal efficiencies in employing only the UV technique without employing the non-thermal plasma technique. In the TiO₂ mediated photo-catalytic reac-

Table 2. The removal efficiency of the VOCs in the TiO₂ mediated photo-catalytic reaction.

| UV wavelength | | 254 nm (2.37*J/l) | 302 nm (1.99* J/l) | 365 nm (1.67* J/l) |
|------------------------------------|--------------------------------|----------------------|-----------------------|-----------------------|
| UV technique only | | 54% | 38% | 36% |
| UV + non-thermal plasma techniques | TiO ₂ Coating (10%) | 48% | 45% | 44% |
| | TiO ₂ Coating (30%) | 71% | 58% | 53% |
| Non-thermal plasma technique only | TiO ₂ Coating (10%) | 53% | | |
| | TiO ₂ Coating (30%) | 78% | | |

*: $\times 10^{-20}$

tions combining the UV and the non-thermal plasma techniques as an initiation method, the highest average removal efficiencies were observed in the combination of UV-254 nm and 30% coating of TiO₂. That is, the best removal efficiency was observed in the combination of a lower UV wavelength and a higher degree of TiO₂ coating. In the TiO₂ mediated photo-catalytic reactions, however, the removal effects (average 71%) at the combination of the UV and the non-thermal plasma were not as good as the removal effects (average 78%) in employing only the non-thermal plasma technique with a higher degree of TiO₂ coating (30% coating). This means that the combination of the UV and the non-thermal plasma as an initiation method in the TiO₂ mediated photo-catalytic reactions was less effective than the technique employing only a non-thermal plasma technique with a high degree of TiO₂ coating in terms of removal effects of the VOCs. It is also inferred that the best way to improve removal efficiencies of the VOCs in the TiO₂ mediated photo-catalytic reactions is to increase a degree of TiO₂ coating with employing a non-thermal plasma technique as an initiation method. That is, increasing TiO₂ surface or coating to be available to the TiO₂ mediated photo-catalytic reaction might be a more economical method for VOC removal as compared with the other initiation methods.

4. CONCLUSIONS

Based on analysis of removal efficiencies of the nine VOC mixtures in the in the TiO₂ mediated photo-

catalytic reactions, the authors could reach the following conclusions:

1. The removal efficiencies of the VOCs under the normal air environment (21% oxygen+78% nitrogen) were much better than those under the nitrogen gas environment containing small amount of oxygen. The higher content of chlorine in the VOC molecules was under the nitrogen gas environment, the lower removal efficiencies of the VOCs might be expected.
2. For the shorter UV wavelength or higher degree of TiO₂ coating, the better removal efficiencies were observed.
3. The removal effects of the VOCs in only UV as an initiation method were the worst among the three initiation methods examined; UV, non-thermal plasma, and a combination of UV and non-thermal plasma.
4. The best removal efficiency of the VOCs, excluding some aldehyde and ketone, was generally observed in the combination of a shorter UV wavelength and a higher degree of TiO₂ coating. However, the removal of VOCs in the combination of the UV and the non-thermal plasma was less effective than that with only a non-thermal plasma as an initiation method.

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