

# DEGRADATION OF SOME CHLOROPHENOLS BY COATED-TiO<sub>2</sub> PHOTOREACTOR

Oh-Jin Jung<sup>†</sup>, Hyung-Il Choi, and Kyung-Hoon Cheong

School of Environmental Engineering, Chosun University, Gwang-ju 501-759, Korea

(received June 2001, accepted November 2001)

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**Abstract** : Three coating procedures, such as CVD, Sol-Gel, and dipping method were used to prepare TiO<sub>2</sub> thin films for degradation of hazardous organic compounds exemplified by chlorophenols. The coating process of TiO<sub>2</sub> onto a quartz glass reactor surface was investigated for improvement of the photodegradation-efficiency. Results of 2-CP degradation followed the order: TiO<sub>2</sub>-thin film photoreactor by CVD/H<sub>2</sub>O<sub>2</sub> > TiO<sub>2</sub> by dipping/H<sub>2</sub>O<sub>2</sub> > TiO<sub>2</sub> by Sol-Gel/H<sub>2</sub>O<sub>2</sub> > TiO<sub>2</sub> by CVD/O<sub>2</sub> > H<sub>2</sub>O<sub>2</sub>-UV only > TiO<sub>2</sub>(suspension)/O<sub>2</sub> > direct UV. It was also observed that the coated TiO<sub>2</sub> reactor could be used to degrade chlorophenols at least up to 60 h without loss of photocatalytic activity. The degradation efficiency increased with decrease of the number of the chlorine atoms substituted on the phenolic ring. The rate of degradation for monochlorophenols was the following order: 2-CP > 4-CP > 3-CP. Also results of chlorophenols degradation followed the order: MCP > DCP > TCP. However, TOC measurements showed that the order of mineralization was the following order: TCP > DCP > MCP.

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**Key Words** : chlorophenols, CVD, immobilization, photodegradation-efficiency, quartz glass tube, Sol-Gel

## INTRODUCTION

In particular, photocatalysis with TiO<sub>2</sub>/UV system has been studied extensively for photo-destruction of organic pollutants. In such a system, the thin films are excited with ultra-violet (UV) or visible light to induce charge separation. The photogenerated holes would then oxidize the organic pollutants. Upon irradiation, the TiO<sub>2</sub> particle generates electron/hole pairs with positive holes(h<sup>+</sup>) in the valance band(vb) and free electron(e<sup>-</sup>) produced in the conduction band(cb).<sup>1)</sup> The holes migrate to the TiO<sub>2</sub> particle surface, and then are reacted with the absorbed water molecules to generate hydroxyl radicals, which can oxidize a host of organic pollutants.

Many researchers have studied the photocatalytic degradation of organic contaminants using large band gap thin film particles.<sup>2~4)</sup> However, although many of contaminants can be totally mineralized to H<sub>2</sub>O and CO<sub>2</sub>, the commercialization TiO<sub>2</sub>/UV process was not successfully achieved. Some investigators have already been used this oxide in an immobilized phase.<sup>5~10)</sup> One promising technique to immobilize this catalyst is achieved by coating the reactor surface with colloidal TiO<sub>2</sub> solution. Serpone and co-worker<sup>11)</sup> used a technique in which a high temperature thermal decomposition of titanium(IV) alkoxide was employed to fix TiO<sub>2</sub> onto the glass beads. The coated TiO<sub>2</sub>-glass beads were used to fill a glass column, as a photoreactor. The authors showed that less than 100 min is enough to totally degrade of 2,4,5-trichlorophenol.

Some other investigators prepared a colloidal

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<sup>†</sup> Corresponding author

E-mail: ojjung@mail.chosun.ac.kr

Tel: +82-62-230-6644, Fax: +82-62-234-6754

solution of titanium(IV) tetraisopropoxide and coated on the surface of the reactor with this colloid solution.<sup>7,9,12,13)</sup> The authors used the same technique to coat the external surface of the immersed glass tube with TiO<sub>2</sub>.

Nevertheless, as described by Zeltner and co-worker,<sup>15)</sup> the photoreactor used by Sabate and co-workers<sup>7)</sup> had several problems. One of them is related with the design of the reactor which have to be specially fabricated. Barbeni et al.<sup>16)</sup> first reported that the photocatalytic oxidation of 4-chlorophenol led to complete mineralization according to the stoichiometry. In the oxidation of 2-chlorophenol and 3-chlorophenol, a complete mineralization was also achieved by D'Oliverira et al.<sup>17)</sup> Barbeni et al.<sup>16)</sup> have studied the degradation of 2,4,5-trichlorophenol using TiO<sub>2</sub> as the photocatalyst. Although hydrogen peroxide has been considered as a strong oxidant, it is still difficult to decompose refractory aromatic compounds such as benzene or phenols using hydrogen peroxide without UV radiation. When UV was applied in the same systems, the reactions lead to fast degradation of these compounds. It has been found that hydrogen peroxide decomposes to water and oxygen without UV irradiation. With UV irradiation, hydrogen peroxide decomposes to the exited hydroxyl radicals. Sundstrom et al.<sup>19)</sup> have studied the UV catalytic oxidation of 2,4,6-trichlorophenol in the presence of hydrogen peroxide.

However, in spite of such an intensive effort, it is still unclear which methods are the most effective to improve the mechanical stability and photocatalytic activity of the thin films. A better TiO<sub>2</sub> surface adhesion technique is necessary to be achieved. By optimizing the catalyst coating procedure, an improvement on the photodegradation technology will also be achieved.

For this purpose, three different coating procedures were investigated, trying to improve the TiO<sub>2</sub> immobilization technique. And the enhance-effects of these photocatalytic activity when some chlorophenols such as 2-chlorophenol, 3-chlorophenol, 4-chlorophenol,

1,3-dichlorophenol, 2,4-dichlorophenol, 2,5-dichlorophenol, 2,4,5-trichlorophenol, 2,3,4-trichlorophenol, 2,4,6-trichlorophenol have been photodecomposed, were discussed in the presence of the H<sub>2</sub>O<sub>2</sub> or O<sub>2</sub> in water.

## MATERIALS AND METHODS

### Materials

TiO<sub>2</sub> (P25) was supplied by Degussa Co., Ridgefield park, NJ. P25 powder has a primary particle size of 40 μm, a specific surface area of 50 ± 1.5 m<sup>2</sup>/g, and its crystalline mode is 20% rutile and 80% anatase type.

The quartz glass tube (QGT: 40.08 π cm<sup>3</sup>) was used as a support to coat the TiO<sub>2</sub> thin films. Titanium tetraisopropoxide (TIP), and series of chlorophenols used in this experiment were purchased from the Aldrich chemical Co. Hydrogen peroxide (ACS reagent grade, 3% solution) was purchased from Eastman Kodak Co. All chemicals were analytical grade and used without further purification. The deionized and double distilled water was used throughout this study. The experimental solutions were subjected to buffered pH solutions of 3 using high concentrated HClO<sub>4</sub> solution.

### Preparation of TiO<sub>2</sub> Thin Films by CVD Method

The preparation of TiO<sub>2</sub> thin films by CVD (chemical vapor deposition) and the thin film characterization were conducted by the methods reported previously.<sup>20)</sup>

### Preparation of TiO<sub>2</sub> Thin Film by Sol-Gel Method

TiO<sub>2</sub> thin film was prepared by photo-reducing TiO<sub>2</sub> onto the support using TIP solution following a method similar to the one described by Toda and Jiangnon.<sup>21,22)</sup>

### Preparation of Thin Film by Colloidal TiO<sub>2</sub>-Dipping

The QGTs of 15 long and 3.3 diameter were used as a coating matrix. These supports were

pre-treated following three procedures. The first QGT was treated with 5%(v/v) HF solution for 12 h. The second QGT was maintained in contact with 4 M NaOH solution for the same period of time. The third QGT was manually scratched with sandpaper #220. These pre-treated QGT reactors were used as supporting surface for the following coating process.

Colloidal TiO<sub>2</sub> was prepared by mixing TIP and 2-propanol in ratio of 1:3 (v/v). The TiO<sub>2</sub> alcoholic mixture was then applied onto the external surface of the reactor. The excess solution was drained and the remaining colloidal TiO<sub>2</sub> was dried at 105 °C for 1 h. The coated reactor was then maintained at 450 °C for 1 h. With one coating, an average of  $1.52 \times 10^{-3}$  g of the catalyst was retained at the surface of the reactor.

### Photoreactor and Light Source

Figure 1 shows the bench-scale photoreactor system in this study. The photoreactor consisted of a cylindrical pyrex-glass cell with the size of 20 cm in diameter and 30 cm in high inside-coated with mirror. The UV light lamp (100 W Hg lamp purchased from the Ace Glass Inc.) was immersed into the solution with the cold air-cooling jacket.

The light intensity was also determined by a Spectronics Model DM-254 UV radiometer. A light intensity of 20.0 watts/m<sup>2</sup> at 365 nm was observed at a distance of one meter above the reactor. The temperature was controlled over

entire irradiation period with air-cooling system. The reaction was quenched by removing the samples from the UV light system because the formation of the main reaction species, hydroxyl radical, needs the presence of UV light.

### Reconditioning of TiO<sub>2</sub>

The TiO<sub>2</sub>-coated reactor used reconditioned by transferring 15% HNO<sub>3</sub> solution into the reactor and keeping it for 15 min. The coated reactor was then thoroughly rinsed with distilled water, and dried at 105 °C.

### Analysis of Organic Compounds

Aqueous solution of the sample (usually 1.0 L) was placed in a photoreactor cell. Prior to irradiation, TiO<sub>2</sub> thin films coated on surface of QGT or TiO<sub>2</sub> powder in water were magnetically stirred in dark for ca. 30 min to establish an adsorption and desorption equilibrium between sample solution and the catalytic surface. At given intervals of illumination, a sample was collected in a test-tube or vial. Aqueous monochlorophenols (MCP) and dichlorophenols (DCP) were treated by following procedure : 5.0 mL of sample was added to 0.1 mL of 1.0 M K<sub>2</sub>CO<sub>3</sub> and 0.5 mL of acetic anhydride. This mixture was allowed to react for 5.0 min under rapid shaking. After this period, 2.0 mL of hexane was introduced and the ester form of MCP and DCP extracted from the aqueous to the organic phase. Trichlorophenols (TCP) were extracted from the aqueous to the organic phase by the following procedure: 5.0 mL of hexane was added to 1.0 mL of a sample containing TCP in concentration between 10<sup>-3</sup> ~ 10<sup>-5</sup> M. These mixture were shaken for 5 min. These two phase were separated and 2 μL (MCP and DCP), or 1 μL (TCP) of the organic phase were injected to a GC/ECD(Hewlett Packard, Model 5890 series II) with a HP-1 column(30 m × 0.53 mm × 0.88 μm-crosslinked methyl silicone gun). The temperature program used was as follows : initial temperature of 60 °C held for 1 min after which the oven temper-

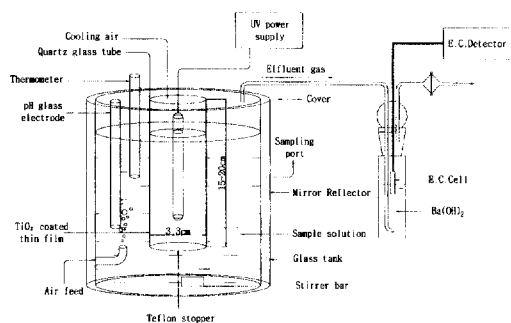


Figure 1. Schematic diagram of photocatalytic reactor for batch experiment.

ature was increased to 200°C at rate of 20°C/min. The final temperature was held for 3 min.

The total organic carbon (TOC) of a sample solution was measured at constant irradiation time intervals using TOC analyzer (Tekmar-Dohrmann, DC-190).

## RESULTS AND DISCUSSION

Figure 2 shows the extent of photodegradation of 2-CP solution when various TiO<sub>2</sub> thin films have been used as a photocatalyst in the presence of oxygen or hydrogen peroxide. Results show that 2-CP degradation follows the order: TiO<sub>2</sub> thin film photoreactor by CVD/H<sub>2</sub>O<sub>2</sub> > TiO<sub>2</sub> by dipping/H<sub>2</sub>O<sub>2</sub> > TiO<sub>2</sub> by Sol-Gel/H<sub>2</sub>O<sub>2</sub> > TiO<sub>2</sub> by CVD/O<sub>2</sub> > only H<sub>2</sub>O<sub>2</sub> > TiO<sub>2</sub>(suspension)/O<sub>2</sub> > direct UV-photolysis. The degradation is fast at the first one-half hour and then becomes slow excepting the suspended TiO<sub>2</sub>/O<sub>2</sub> and direct photolysis.

In Figure 2, the degradation power of illuminated hydrogen peroxide alone is sufficient to destroy, in 3 h, 74% of initial 2-CP, while the system combining H<sub>2</sub>O<sub>2</sub> and TiO<sub>2</sub> coated photoreactor by Sol-Gel degraded 85% of the same compound. As a comparison, TiO<sub>2</sub> thin films was prepared by CVD method. After 3 h of irradiation, 99% of initial 2-CP was destroyed by the system using TiO<sub>2</sub> thin films in combination with hydrogen peroxide. The same figure shows that in absence of H<sub>2</sub>O<sub>2</sub>, only 40% of 2-CP is degraded within the same time period. These results show that TiO<sub>2</sub> thin films have the capability to degrade 2-CP, however, in absence of hydrogen peroxide, a slight difference in the degradation efficiency is observed between the use in TiO<sub>2</sub> thin film photoreactor coated by Sol-Gel, dipping or CVD method. Especially, efficiency of photodegradation for the photoreactor coated by CVD was better than that for photoreactor coated by Sol-Gel or dipping method. Hence, these results show that the surface-characteristics of TiO<sub>2</sub> thin films play an important role on the photocatalytic efficiency.<sup>23)</sup>

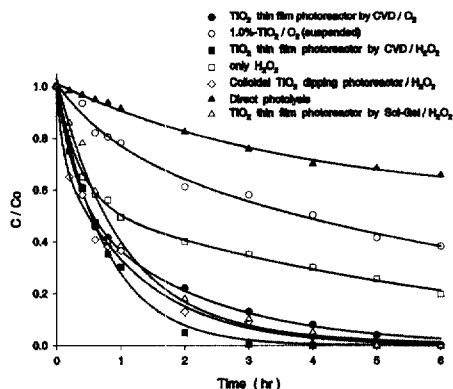


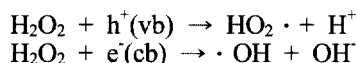
Figure 2. Photodegradation of 2-CP using various photoreactor types. Initial concentration: 10<sup>-3</sup> M 2-CP, pH 3.0, 10<sup>-1</sup> M H<sub>2</sub>O<sub>2</sub>, and 5.0 × 10<sup>-2</sup> M NaClO<sub>4</sub>.

As mentioned above, the thin film prepared by dipping of colloidal TiO<sub>2</sub> observed that the TiO<sub>2</sub> thin film coated on the glass surface was very strong. The number of dipping by colloidal TiO<sub>2</sub> that could be applied onto the surface increased as the coating layer increased. With five dipping of the coating solution, the reactor surface was totally covered with TiO<sub>2</sub>. However, increasing the number of coating layers from five to six led to some problems. The TiO<sub>2</sub> film that once smooth, started to show some cracks by increasing the number of layers the coated surface began to peel off. These results show that the optimum conditions were obtained with five coating layers of the colloidal TiO<sub>2</sub> solution.

The structural characterization of thin films coated by CVD and Sol-Gel or dipping method, and its effect on the photochemical properties have been studied to understand the photocatalytic degradation of 2-CP. The great enhancement of the photocatalytic properties above 400°C was a result of crystallization of TiO<sub>2</sub>, while thin film coated by the Sol-Gel or colloidal TiO<sub>2</sub> dipping method showed its amorphous structure having the poor photo-effect below this temperature. Moreover, most contribution for the area increase from the crystallite surface.<sup>20)</sup> In the CVD sample, the nanometer size of grains can provide large

surface area that is the guarantee for the activity improvement. This uniformity of the distribution and TiO<sub>2</sub> mono-crystallite dose provide large surface area and enhance activity of photocatalyst. While, TiO<sub>2</sub> thin films prepared by Sol-Gel or colloidal TiO<sub>2</sub> dipping method have an amorphous structure and its structure is cracked. In this study, the degradation is fast at the one-half hour and then becomes slow. Even with longer irradiation time, up to 6 h, 7.2% of the initial 2-CP was still in solution in the process of photodegradation using TiO<sub>2</sub> thin film prepared by dipping method in the absence of H<sub>2</sub>O<sub>2</sub>. It was concluded that although the bond between the glass surface and the TiO<sub>2</sub> was strong enough, the degradation capacity of this coated TiO<sub>2</sub> reactor was not satisfactory. Therefore, the photocatalytic efficiency of TiO<sub>2</sub> thin film by CVD is better than the thin films by Sol-Gel or colloidal TiO<sub>2</sub> dipping method in the process of photodegradation for some chlorophenols in water.

In the presence of TiO<sub>2</sub> thin film-hydrogen peroxide system, about 50% of 2-CP was destroyed within the 30 min of photoreaction. The increase in the degradation efficiency is a result of photolysis of H<sub>2</sub>O<sub>2</sub> which increases the concentration of hydroxyl radicals as below.<sup>24)</sup>



In the blank run, no significant degradation, less than 5%, was observed by direct photolysis. Another fact that needs to be cited is that H<sub>2</sub>O<sub>2</sub> alone under UV irradiation was able to degrade about 45% of the initial 2-CP in the first hour, however about 77% of 2-CP was only degraded at the end of 6 h in the same experimental condition. To compare the efficiencies of the TiO<sub>2</sub> coated photoreactors prepared by CVD method, this study was performed using the TiO<sub>2</sub> thin film photoreactor coated by CVD in absence or presence of H<sub>2</sub>O<sub>2</sub> in water.

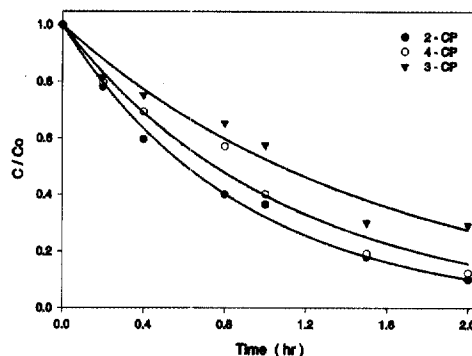


Figure 3. Photodegradation of monochlorophenols using TiO<sub>2</sub> thin film photoreactor prepared by CVD method. Initial concentration: 10<sup>-3</sup> M MCP, pH 3.0, and 5.0 × 10<sup>-2</sup> M NaClO<sub>4</sub>.

In TiO<sub>2</sub>-QGT-CVD/H<sub>2</sub>O<sub>2</sub>-UV system, this result (Figure 2) shows the best degradation efficiency. Especially 99% of 2-CP in this system was degraded within 120 min. These results showed that chlorophenols can be photodegraded using the coated TiO<sub>2</sub> system. However, the degradation efficiency is enhanced when H<sub>2</sub>O<sub>2</sub> is introduced to the system.

In this study, a reactor coated with TiO<sub>2</sub> by CVD method was used to oxidize chlorophenols. Figures 3, 4, and 5 show the degradation results of MCP, DCP and TCP. These were degraded more than 90% within 2 h of irradiation. The results show that this degradation follows the order: 2-CP > 4-CP > 3-CP.

From the results of photodegradation of DCP (Figure 4), it was observed that within 2 h of photoreaction, 90% of initial 2,3-DCP and 2,4-DCP concentrations was degraded. Nevertheless, the degradation efficiency of all other DCP was considerably high, ranging between 65% to 85% within 2 h of irradiation. Huang and co-workers<sup>24)</sup> have also observed that a longer period of irradiation was necessary to degrade DCP compared to MCP.

For TCP (Figure 5), it can be seen that the degradation efficiency of TiO<sub>2</sub> thin film reactor coated by CVD method was very similar to the results observed for DCP. The results show that this degradation follows the order:

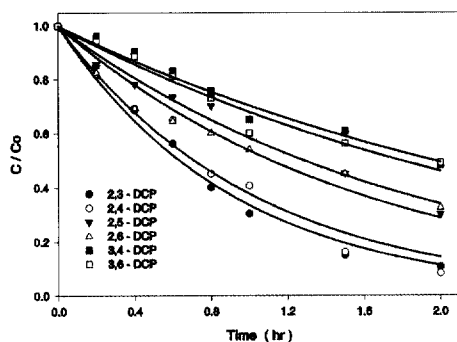


Figure 4. Photodegradation of dichlorophenols using the  $\text{TiO}_2$  thin film photoreactor prepared by CVD method. Initial concentration:  $10^{-3}$  M DCP, pH 3.0, and  $5.0 \times 10^{-2}$  M  $\text{NaClO}_4$ .

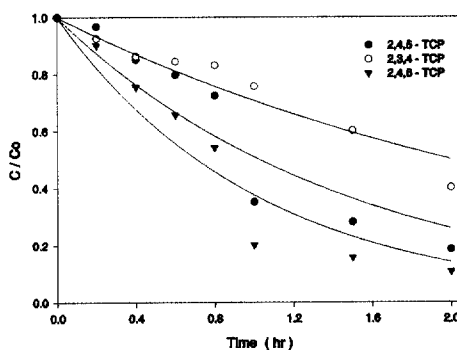


Figure 5. Photodegradation of trichlorophenols using the  $\text{TiO}_2$  thin film photoreactor prepared by CVD method. Initial concentration:  $10^{-3}$  M TCP, pH 3.0, and  $5.0 \times 10^{-2}$  M  $\text{NaClO}_4$ .

2,4,6-TCP > 2,4,5-TCP > 2,3,4-TCP. The degradation efficiency was ranged between 60% to 90% within 2 h of photoreaction.

A more detailed degradation study was performed for 4-CP, 2,4-DCP, and 2,3,6-TCP. Total degradation of 4-CP was achieved within 2 h of irradiation (Figure 6). However, results from the organic carbon analysis (TOC) showed that only about 50% of the initial organic carbon was mineralized to  $\text{CO}_2$ .

Also Figure 6 shows the results of the photodegradation of 4-CP and 2,4-DCP. In both cases, total degradation of the original organic compounds was achieved within about 2 h of irradiation. However, TOC measurements

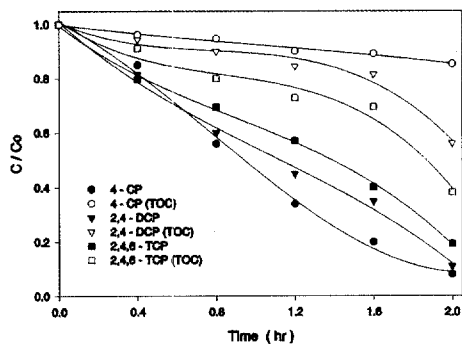


Figure 6. Comparison between photodegradation of chlorinated phenols using the  $\text{TiO}_2$  thin film photoreactor prepared by CVD method and its TOC data. Initial concentration:  $10^{-3}$  M sample, pH 3.0, and  $5.0 \times 10^{-2}$  M  $\text{NaClO}_4$ .

show that mineralization was not reached at the same period of time. From TOC analysis the order of mineralization was follows: TCP > DCP > MCP.

The results in Table 1 also show that in general, monochlorophenols are easier to degrade than dichlorophenols or trichlorophenols. The order of the degradation of the chlorinated phenols can be generalized as follows:  $\text{Cl}_1 > \text{Cl}_2 \geq \text{Cl}_3$ . Alberici and Jardim<sup>25)</sup> also mentioned the same order, in which they pointed out that the degradation of dichlorophenols were faster than trichlorophenols.

As shown in Figures 4 and 5, within 2 h of irradiation, a considerable wide range of degradation percentage was observed for both groups of dichlorophenols and trichlorophenols. Therefore, in general, the degradation of dichlorophenols are slightly faster than trichlorophenols.

The degradation efficiency increases as the number of the chlorine atoms substituted on the phenolic ring decreases. These results indicate that chloride ions, which are one of the final products of the degradation process, are affecting the efficiency of the system. It was suggested that chloride ions could replace the hydroxyl radicals attached to the  $\text{TiO}_2$  surface as follows :

Table 1. Initial rate constant( $r_0$ ) and  $t_{1/2}$  observed for the degradation of monochlorophenols, dichlorophenols, and trichlorophenols using TiO<sub>2</sub> thin film photoreactor prepared by CVD method

Compound	$r_0$ (M/min)	$t_{1/2}$ (min)
2-CP	$1.83 \times 10^{-5}$	30
3-CP	$0.87 \times 10^{-5}$	57
4-CP	$1.51 \times 10^{-5}$	45
2,3-DCP	$0.82 \times 10^{-5}$	56
2,4-DCP	$0.79 \times 10^{-5}$	81
2,5-DCP	$0.72 \times 10^{-5}$	85
2,6-DCP	$0.63 \times 10^{-5}$	87
3,4-DCP	$0.33 \times 10^{-5}$	93
3,6-DCP	$0.67 \times 10^{-5}$	85
2,3,4-TCP	$0.40 \times 10^{-5}$	89
2,4,5-TCP	$0.80 \times 10^{-6}$	94
2,4,6-TCP	$1.33 \times 10^{-6}$	102



As the concentration of the generated Cl<sup>-</sup> ion increases, more hydroxyl radicals are replaced on the surface of the thin film. Consequently the degradation efficiency decreases. Similar inhibition caused by chloride ions was also observed by Kormann and co-worker<sup>26)</sup> and by Pruden and Ollis.<sup>27)</sup> One compound from each chlorophenol group was chosen for further studies on the mineralization efficiency of TiO<sub>2</sub> thin film reactor. The extent of mineralization was monitored by TOC analysis. The high values of TOC observed in Figure 6 can be explained by the formation of degradation intermediates. In the present work, the identification of any possible intermediate was not pursued.

The evidence obtained total carbon dioxide and chloride ion measurements suggests that photocatalytic degradation of all kinds of chlorophenols in this study, follow mineralization pathways in which several intermediate steps, such as hydroxylation and ring-cleavage reaction involved,<sup>28)</sup> and this clearly indicates that the photocatalytic oxidation process including TiO<sub>2</sub> thin film-CVD, coated-TiO<sub>2</sub>-Sol-Gel,

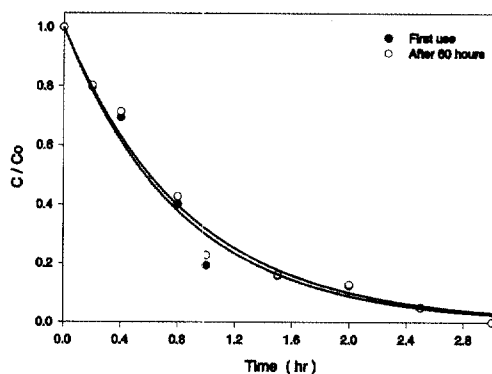


Figure 7. Photodegradation of 4-CP using TiO<sub>2</sub> thin film photoreactor prepared by CVD method with zero and 60 h of use. Initial concentration:  $10^{-3}$  M 4-CP, pH 3.0, and  $5.0 \times 10^{-2}$  M NaClO<sub>4</sub>.

and colloidal TiO<sub>2</sub> dipping photoreactor system is effective in completely mineralizing the chlorinated organic compounds to CO<sub>2</sub> and Cl<sup>-</sup> ions within at least 4 h in the presence of air.

Some investigator have already identified and quantified some of these compounds.<sup>28-29)</sup> The main intermediates were identified as catechol, 2-chlorocatechol, 4-chlororesocinol, chlorohydroquinone, and organic acids such as glyoxalic acid, succinic acid, malic acids, oxalic acid, and acetic acid. It is believed that the same intermediates were formed in this experiment.

Figure 7 shows that the photocatalytic efficiency of TiO<sub>2</sub> thin film photoreactor by CVD did not decrease even after 60 h of use. It is important to mention that all the studies of 4-CP degradation were performed using the same photoreactor. Therefore, between the first and the one with 60 h of use, many different chlorophenols were employed as target compounds. Nevertheless, the efficiency of the TiO<sub>2</sub> coated photoreactor did not change with this extensive use.

## CONCLUSIONS

In this study, three different coating procedures were investigated to improve the TiO<sub>2</sub>

immobilization technique. The enhance-effects of these photocatalytic activity were discussed in the presence of the  $H_2O_2$  or  $O_2$  in water. Three coating procedures, such as CVD, Sol-Gel, and dipping method were used to prepare thin films,  $TiO_2$ -QGT, for degradation of hazardous organic compounds exemplified by various chlorophenols.

The thin films prepared by CVD, Sol-Gel or dipping method did not easily remove from the coated surface. The photodegradation efficiency of these coated reactors was considerably high. The same photoreactor was used for the degradation experiments of all chlorophenols, and the photodegradation efficiency of coated reactor was not affected by its reuse.

The photodegradation efficiency of catalysts prepared by these three methods mentioned above, is much more increased than one of the  $TiO_2$ (suspension)-UV system. The degradation efficiency of organic compounds using coated- $TiO_2$ -UV system is also increased by adding hydrogen peroxide.

In these three different thin films, although total mineralization to inorganic carbon was not achieved at that time interval, total degradation of the studied organic compounds was observed in general within about 3 h of irradiation. The degradation efficiency increases with decrease of number of the chlorine atoms substituted on the phenolic ring.

## ACKNOWLEDGEMENT

This study was supported by research funds from Chosun University, 1999.

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