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Photocatalytic ozonation of 2, 4-dichlorophenoxyacetic acid in water with a new TiO_2 fiber

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ABSTRACT: More effective techniques are required to mineralize the increasing number of recalcitrant organic contaminants at low concentrations in the water environment using advanced oxidation process. Though relatively new, photocatalytic ozonation (O_3/UV/TiO_2) is considered superior to ozonation (O_3) and photocatalysis (UV/TiO_2), due to synergistic effects and use of immobilized TiO_2 photocatalysts is a milestone in advance oxidation process. This article aimed to elucidate 2, 4-dichlorophenoxyacetic acid (2, 4-D) mineralization characteristics in low aqueous solutions by O_3/UV/TiO_2 using the world's first high-strength TiO_2 fiber catalyst in laboratory experiments. 2, 4-D degradation and TOC removal in O_3, UV/TiO_2 and O_3/UV/TiO_2 followed pseudo-first order reaction kinetic. The removal rates for 2, 4-D and TOC in O_3/UV/TiO_2 were respectively about 1.5 and 2.4-fold larger than the summation of the corresponding values in O_3 and UV/TiO_2. The O_3/UV/TiO_2 process was characterized by short-lived few aromatic intermediates, faster degradations of aliphatic intermediates and dechlorination as a major step in 2, 4-D mineralization. The significantly enhanced 2, 4-D mineralization in the process was attributed to increased ozone decomposition and reduced electron-hole recombination on TiO_2 surface resulting to a large number of $^{\cdot}OH$ generation. The O_3/UV/TiO_2 process with the TiO_2 fiber catalyst was very promising with respect to the major challenges being faced in AOP involving TiO_2, namely separation of powder catalyst in suspension and reduced efficiency of immobilized catalysts (e.g. TiO_2 film/fiber).

Key words: *Photocatalysis, degradation, hydroxyl radical, intermediates, rate constant, total organic carbon*

INTRODUCTION

Ever-increasing use of chemicals and discovery of new recalcitrant organic contaminants in water environment have remained as major challenges in developing effective treatment methods for water and wastewater. A large number of organic contaminants are hazardous even at low concentration levels and stringent regulations are being enforced, especially in the industrialized nations for both conventional and non-conventional pollutants. Therefore, more effective methods are necessary for treating contaminated water and wastewater to meet the challenges. Ozonation (O_3) and photocatalysis (UV/TiO_2) are widely investigated advanced oxidation processes (AOP) for treating contaminated waters (Djebbar and Sehili, 1998; Yao, *et al.*, 1998; Drzewicz, *et al.*, 2004; Singh and Muneer, 2004). Ozonation alone is less effective, since its reaction with organic contaminants is selective (Brillas, *et al.*, 2003; Agustina, *et al.*, 2005; Li, *et al.*, 2005) and generation of free radicals from its decomposition takes place only at elevated pH conditions (Munter, 2001). Oxidation of contaminants in UV/TiO_2 system involves free hydroxyl radical ($^{\cdot}OH$), but separation of TiO_2 catalyst in suspension has been a major obstacle. Although recent developments in TiO_2 film and fiber catalysts can overcome the problem, mere photocatalysis is reported to be less efficient for several organic contaminants (Agustina, *et al.*, 2005; Li, *et al.*, 2005; Terashima, *et al.*, 2006). Photocatalytic ozonation (O_3/UV/TiO_2) is emerging as a more promising oxidation method for refractory organic contaminants due to a large number of $^{\cdot}OH$ generation (Agustina, *et al.*, 2005; Beltran, *et al.*, 2005; Li ,*et al.*, 2005; Farre, *et al.*, 2005). Few literatures are available on the O_3/UV/TiO_2 process,because its use is relatively new, while successful use of TiO_2 fiber catalyst is expected to be

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a milestone in practical applications of the UV/TiO_2 and O_3/UV/TiO_2 processes. This article aimed to investigate degradation characteristics of low concentration (≈ 45 μM) 2, 4-dichlorophenoxyacetic acid (2, 4-D) in aqueous solution by the O_3/UV/TiO_2 process using the world's first high-strength TiO_2 fiber catalyst (Ishikawa, 2004) developed by Ube Industries Ltd., Japan, with laboratory batch-experiments.

MATERIALS AND METHODS

The 2, 4-D standard (Cica-Reagent) was obtained from Kanto Chemical Co., Inc. Na_2SO_3 solution (1.0 g/L) and Spectroquant® Picco Colorimeter test kit (Merck, Germany) which were respectively used to quench and measure residual dissolved ozone in samples in O_3 and O_3/UV/TiO_2 experiments. Other reagents were of HPLC grade obtained from Wako Pure Chemicals Ltd., Japan. Carrier gas flow from ozone generator to reactor was regulated with a flow meter, while O_3 concentration in the carrier gas was continuously monitored using an ozone measuring device (EG-600, EBARA JITSUGYO Co. Ltd., Japan). A Pyrex glass reactor (8.0 l capacity, ID: 18.4 cm, h: 30 cm) with centrally placed tubular jacket (OD: 6.2 cm) and six circular ports (OD: 2.8 cm) at the top was used for batch experiments. TiO_2 fiber catalyst (20 cm × 25 cm sheets) was supplied by Ube Industries Ltd., Japan. A cylindrical catalyst module (OD: 18.4 cm, h: 30 cm) was prepared using the catalyst and stainless steel wire mesh (3 mm × 3 mm opening). Ozone was generated by passing air (21% O_2 + 79% N_2) through an ozone generator (Nippon Ozone Co., Ltd.). A UV tube lamp (10 W, 254 nm, UVL10DL-12, SEN Lights Corporation, Japan) was the source of irradiation in UV/TiO_2 and O_3/UV/TiO_2 processes. Headspace gas in the reactor was continuously pumped, dried and passed through a packed tower to absorb residual O_3 gas.

Seven and half liter of about 45 μM 2, 4-D solution without initial pH adjustment was poured into the reactor. Ozone generator, carrier gas flow meter, ozone concentration monitoring device, reactor, pump and absorption tower were connected in series. The solution was continuously mixed with a magnetic stirrer with the same speed in all the experiments. The samples were taken at 20 min. interval for analysis, while all of the experiments were carried out for a duration of 2 h. The catalyst module was placed inside the reactor in the UV/TiO_2 and O_3/UV/TiO_2 experiments. Carrier gas flow rate and ozone concentration in it were respectivly maintained at 1.0 L/min. and 2.0 mg/L throughout the experiments in the O_3 and O_3/UV/TiO_2 processes. The ozone concentration in carrier gas was regulated by varying electric voltage in ozone generator.

The samples were analyzed for remaining 2, 4-D and both aromatic and aliphatic intermediates using HPLC with UV detector (Model: D-7000, Hitachi, Japan). Inertsil ODS-3V column (150 mm × 3 mm ID × 5 μm) with 35 °C oven temperature, 20 μL sample volume and CH_3CN: H_2O: CH_3COOH = 50: 49: 1 (v/v) mobile phase at 0.40 mL/min. flow rate was employed for aromatic intermediates including 2, 4-D at 254 nm. Supelcogel C-610H (30 cm × 7.8 mm ID × 9 μm) together with Supelguard C-610H (5 cm × 4.6 mm ID) columns with 30 °C oven temperature, 20 μL sample volume and 0.1% H_3PO_4 in water (v/v) mobile phase at 0.50 mL/min. flow rate were used for aliphatic intermediates at 210 nm. The detected intermediates of 2, 4-D oxidation were identified by matching peak retention time (RT) of oxidized 2, 4-D samples with the peaks of various known standards. Total organic carbon (TOC) analyzer (TOC-$V_{CSH,}$ Shimadzu, Japan) was used to measure TOC while Ion Chromatograph with conductivity detector (Model: L-7000, Hitachi, Japan), GL-IC-A25 column (150 mm × 4.6 mm ID), 40 °C oven temperature and 4.0 mM Na_2CO_3 solution (in water) mobile phase at 1.0 mL/min. flow rate were used to measure chloride ion concentration in the samples. Residual aqueous phase ozone in the samples was measured by photometric diphenylen-diamine-based (DPD) method at 528 nm UV wave length.

RESULTS AND DISCUSSION

All the experiments were carried out in triplicate and average values of the results are presented in figures while the error bars in the figures indicate standard deviations. Average initial pH values of about 45 μM 2, 4-D solutions in O_3, UV/TiO_2 and O_3/UV/TiO_2 processes were 4.36, 4.32 and 4.33, respectively, which gradually decreased during a 2 h. oxidation. The O_3/UV/TiO_2 and UV/TiO_2 processes have the most and least efficiencies respectively for 2, 4-D oxidation (Fig. 1). About 54% and 83% of 2, 4-D was oxidized in UV/TiO_2 and O_3 at the end of the 2 h. oxidation, while one hundred percent of the 2, 4-D degraded in less than two hours in O_3/UV/TiO_2. The half-life periods for 2, 4-D in the O_3, UV/TiO_2 and O_3/UV/TiO_2 processes were about 60, 110 and 28 min., respectively. 2, 4-D oxidations in all of the three processes were well-

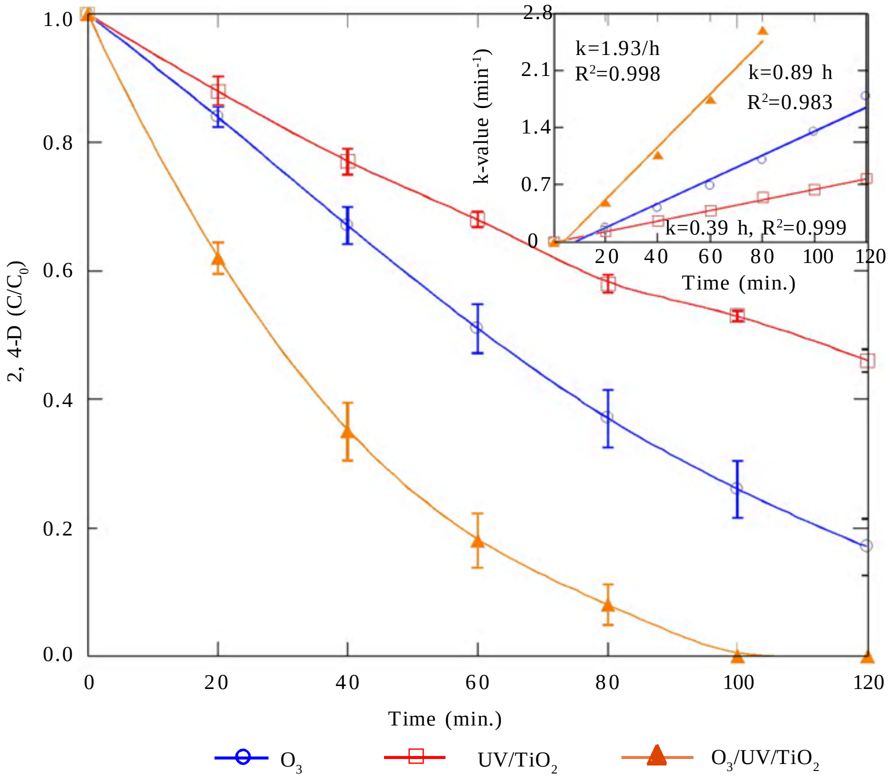

Fig. 1: Relative 2, 4-D concentration profiles in different oxidation systems

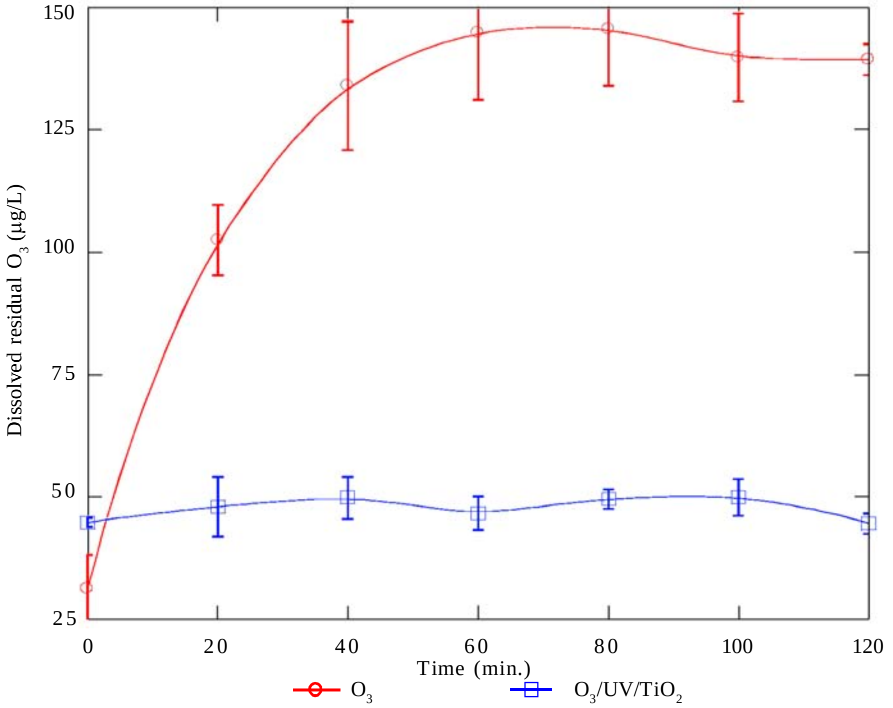

Fig. 2: Residual dissolved ozone concentration profiles during 2, 4-D mineralization

described by pseudo-first order reaction kinetic (Fig. 1). The degradation rate (k) values in UV/TiO_2, O_3 and O_3/UV/TiO_2 were 0.39, 0.89 and 1.93/h, respectively. The value for O_3/UV/TiO_2 was about 1.5 times higher than the summation of the values for the other two processes. Thus, O_3/UV/TiO_2 using TiO_2 fiber catalyst was found to be a very effective process to degrade the model pollutant in low aqueous solution. Though a positively charged hole on TiO_2 surface in UV/TiO_2 process is mentioned to possess the highest oxidation power (Munter, 2001), its role on oxidation of micropollutants is not well explained. Therefore, ·OH is considered to be the sole oxidizing species, which has the second highest oxidation power (Munter, 2001). Despite the non-selective reaction and high oxidation power of ·OH, UV/TiO_2 with fiber catalyst was found to be rather a slow process in this investigation, which is consistent with the earlier results with TiO_2 fiber, powder and film catalysts (Beltran, *et al.*, 2005; Li, *et al.*, 2005; Terashima, *et al.*, 2006). Generation and utilization of ·OH are two important steps in oxidations involving ·OH. However, the quantification of ·OH in a process is quite complicated due to its very short life. Chloride ions at high concentrations are reported to have scavenging effect on ·OH (Kiwi, *et al.*, 2000). Theoretically, about 90.48 μM of chloride ions can be liberated from 45 μM of 2, 4-D oxidation. Photocatalytic oxidation experiments with 45 μM 2, 4-D, TiO_2 fiber catalyst and various initial chloride ion concentrations (0, 56, 85, 113 and 141 μM) were also carried out. The results (not shown) exhibited no significant effect of chloride ions on 2, 4-D oxidation. The slow 2, 4-D oxidation in the UV/TiO_2 process was presumably due to a less number of ·OH generation. Recombination of electrons and positive holes formed on TiO_2 surface are considered as a possible reason for a less number of ·OH in the process (Agustina, *et al.*, 2005; Farre, *et al.*, 2005). The 2, 4-D degradation rates in O_3 and O_3/UV/TiO_2 were about 2.3 and 4.9 times of UV/TiO_2, while the value for O_3/UV/TiO_2 was about 2.2 times of O_3. Since the oxidations took place below 4.36 pH value in the O_3 process, direct ozonation of 2, 4-D was most likely a major degradation mechanism (Beltran, *et al.*, 2005). The enhanced degradation in O_3/UV/TiO_2 can be attributed to ozone decomposition resulting in an increased ·OH production (Agustina, *et al.*, 2005; Beltran, *et al.*, 2005). Dissolved residual ozone concentrations in O_3/UV/TiO_2 were significantly smaller than that in O_3 and almost constant throughout the experiments (Fig. 2). This presumably is the result of its decomposition, while the values in the O_3 process drastically increased during the first-half of the experiment and then remained almost stagnant. Farre, *et al.*, (2005) also argued that the presence of dissolved ozone in irradiated TiO_2 aqueous suspension not only increases ·OH production but also decreases the recombination of electrons and positive holes on the TiO_2 surface.

Since all the detected intermediates were not identified, their abundance profiles with time are used for discussion in this section. Ozonation was characterized by the largest number of intermediates including eight aromatics (Fig. 3) and ten aliphatics (Fig. 4). The two identified aromatics (2, 4-dichlorophenol (2, 4-DCP) and benzyl alcohol (BA)) were relatively at low concentrations while the two unknowns (RT ≈ 4.5 and 6.6 min.) appeared to be the main (Fig. 3). The least number of intermediates was detected in the UV/TiO_2 process (Fig. 5), where 2, 4-DCP was the main aromatic intermediate while benzyl alcohol at low concentrations was also detected at the end of the experiments. Maleic acid and one unknown (RT ≈ 15.1 min.) were aliphatic intermediates in the process. Three aromatics (2, 4-DCP, BA and one unknown (RT ≈ 4.1 min.)) and nine aliphatics, including the four unknowns (Fig. 6), were detected in the O_3/UV/TiO_2 process, where the number was larger than that in UV/TiO_2 and smaller than that in O_3. 2, 4-DCP, which is more toxic than the parent compound and was the major aromatic byproduct in the UV/TiO_2 process. Despite increased toxicity due to the 2, 4-DCP formation, the least number of intermediates may be interpreted as a result of shorter paths for 2, 4-D degradation. The increasing intensity profiles of both aromatic and aliphatic intermediates until the end of the experiments (Fig. 5) exhibited that UV/TiO_2 is a slow process in terms of 2, 4-D mineralization. In contrast to UV/TiO_2, most of the aromatic intermediates detected in ozonation reached to their highest intensity values, and then decreased before the end of the experiments (Fig. 3). But the intensity values for all of the aliphatic intermediates continued its increasing to the end (Fig. 4). The largest number of aliphatic intermediates was attributed to the selective reaction of ozone at acidic or neutral pH conditions resulting in the formation of carboxylic acids as the end products (Agustina, *et al.*, 2005). The slow degradations of the carboxylic acids were also presumably due to the

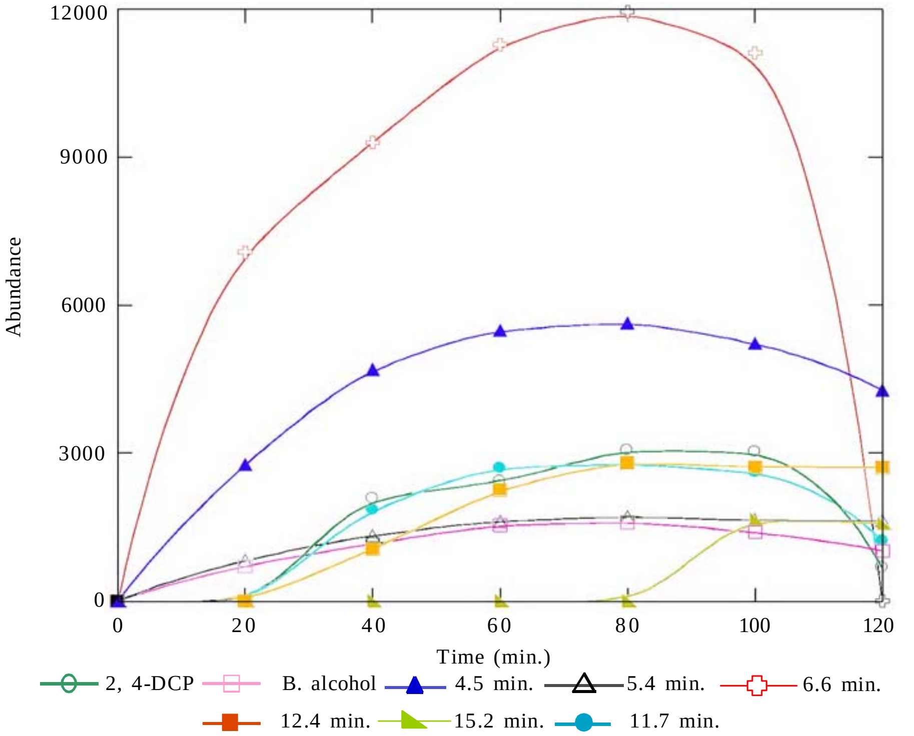

Fig. 3: Aromatic intermediates detected in ozonation of 2, 4-D

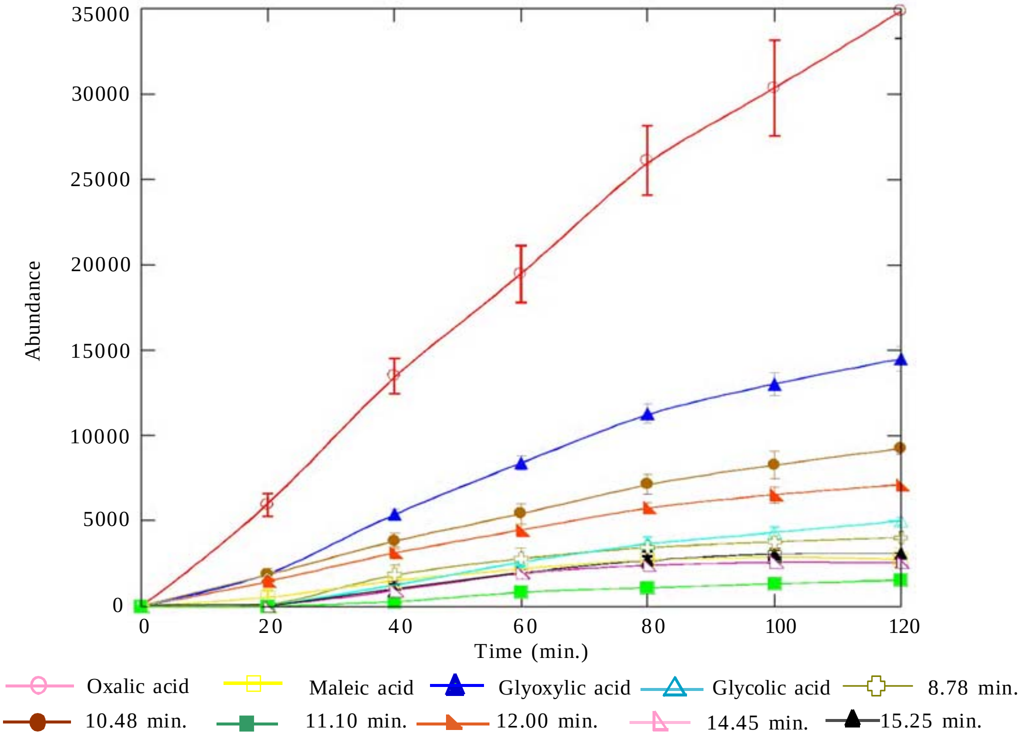

Fig. 4: Aliphatic intermediates detected in ozonation of 2, 4-D

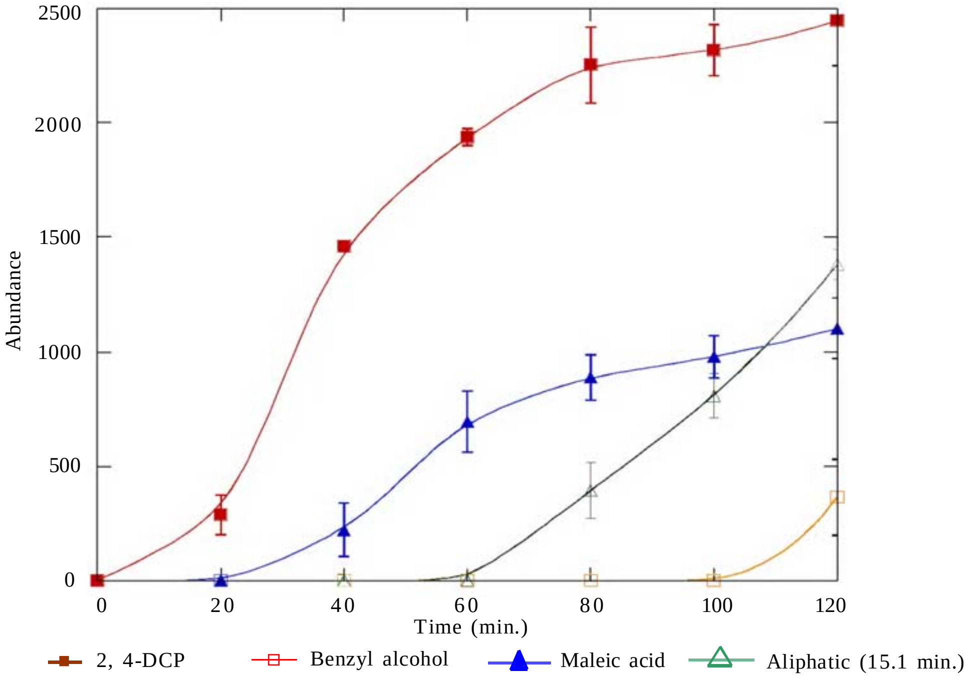

Fig. 5: Intermediates detected in photocatalytic oxidation of 2, 4-D

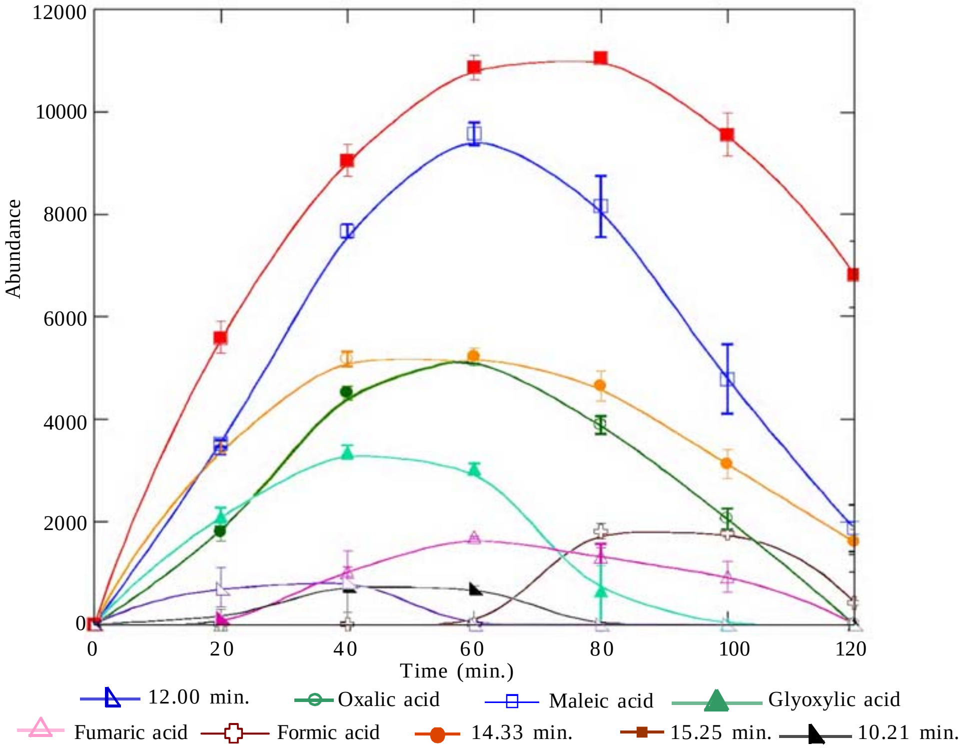

Fig. 6: Aliphatic intermediates detected in photocatalytic ozonation of 2, 4-D

selective reaction. Though several aliphatic intermediates were not identified (Fig. 4), the formation of saturated carboxylic acids in the process could have resulted in the slow oxidation, since the unsaturated carboxylic acids are relatively unstable and get oxidized more easily than the saturated ones (Jung, 2001). Low concentrations of the three aromatic intermediates in O_3/UV/TiO_2 (not shown) were present for a short period indicating their fast oxidations. Despite a relatively large number of aliphatic intermediates in the process, their intensities reached to the peak values at the middle of the experiments and decreased significantly by the end (Fig. 6). Thus, the detected intermediates in the O_3/UV/TiO_2 process were oxidized faster than that in the other two processes presumably due to the increased ·OH generation and its effective use in the oxidation. In contrast to ozonation, the nature of aliphatic intermediates did not appear to be an important factor for their oxidation in the O_3/UV/TiO_2 process.

Though 2, 4-D oxidation in O_3 was more than two folds larger than that in UV/TiO_2, no significant difference in TOC removals between these two processes was observed through the first half of the experiments (Fig. 7). Ozonation then appeared to be less efficient compared to UV/TiO_2 and the difference between them gradually increased till the end. TOC removals in these processes by the end of the experiments were about 17% and 23%, respectively. Similar to 2, 4-D degradation, O_3/UV/TiO_2 was the most effective in terms of TOC removal among the three processes (Fig. 7), where the removal was about 67% at the end of the 2 h. oxidation. But the O_3 and UV/TiO_2 processes appeared to be very inefficient in terms of TOC removal. TOC removals by the three processes were well described by pseudo first-order reaction kinetic (inset of Fig. 7). The removal rate k values for O_3, UV/TiO_2 and O_3/UV/TiO_2 were about 0.09, 0.14 and 0.56/h, respectively. The k value for O_3/UV/TiO_2 was about 2.4 folds higher than the summation of k values for the remaining two processes. Thus, 2, 4-D mineralization in the O_3/UV/TiO_2 process using TiO_2 fiber catalyst was very effective due to the synergistic effects of photocatalysis and ozonation. Two possible mechanisms are proposed for the enhanced mineralization of organics in the combined process (Agustina, *et al.*, 2005). Dissolved ozone can easily accept electrons produced on TiO_2 surface, which reduces the possibility of their recombination with positive holes resulting in a large number of ·OH formation. A large number of hydrogen peroxide and ·OH can also be produced from dissolved ozone as a result of UV irradiation. More than one parallel path for ·OH generation is proposed in the combined process (Beltran, *et al.*, 2005).

Though ozone photolysis is a slow process in the beginning, it is considered to be an important mechanism for ·OH generation after a few minutes. With high extinction coefficient value of ozone at 254 nm wave length (ε = 3300/M/cm), a significantly large number of ·OH is generated from its photolysis (Munter, 2001). The presence of TiO_2 implies some adsorption steps followed by surface reactions though there is a lack of kinetic information (Beltran, *et al.*, 2005). Reaction between ozone and titanium yields adsorbed ozonide ion radical ($O_3^{-\cdot}$), which is another source of ·OH. Thus, three parallel paths of ·OH generation are available in the O_3/UV/TiO_2 process in addition to direct photolysis and ozonation of 2, 4-D and its intermediates. The almost constant and significantly smaller dissolved residual ozone values for the process (Fig. 3) were presumably the result of ozone photolysis and/or adsorption followed by its decomposition. Reactions of organics containing C-H or C-C multiple bonds with ·OH generally proceed with larger rate constants (~ 10^{10}/M/S) and therefore their oxidations are usually limited by ·OH generation and reaction with ·OH scavengers (Haag and Yao, 1992). Carbonate, bicarbonate and high concentrations of chloride ions are considered as ·OH scavengers, but their scavenging effects in these experiments were presumably insignificant. Reaction rates of ozone with aromatics including phenols are very small (by 6 ~ 11-log orders) compared to ·OH (Munter, 2001). Therefore, the generation of a large number of ·OH from the parallel paths and high reaction rates of ·OH with 2, 4-D and its degradation intermediates presumably resulted in the enhanced 2, 4-D mineralization in the O_3/UV/TiO_2 process.

The chloride content in hazardous organics is considered as a measure of their toxicity and hence dechlorination is a very important step in their oxidations. Dechlorination in a sample was calculated as the ratio of free chloride ion concentration in the sample to the theoretical chlorine content in 2, 4-D before oxidation. Dechlorination profiles for the three oxidation processes in this investigation (Fig. 8) exhibited that O_3 was more efficient than UV/TiO_2 and

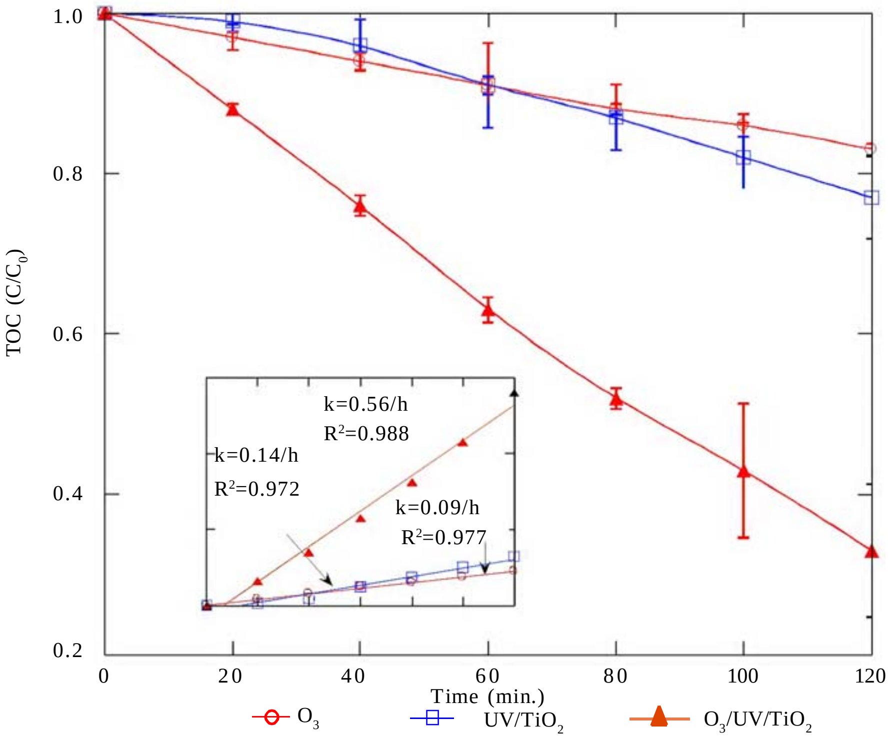

Fig. 7: Relative TOC concentration profiles during 2, 4-D mineralization

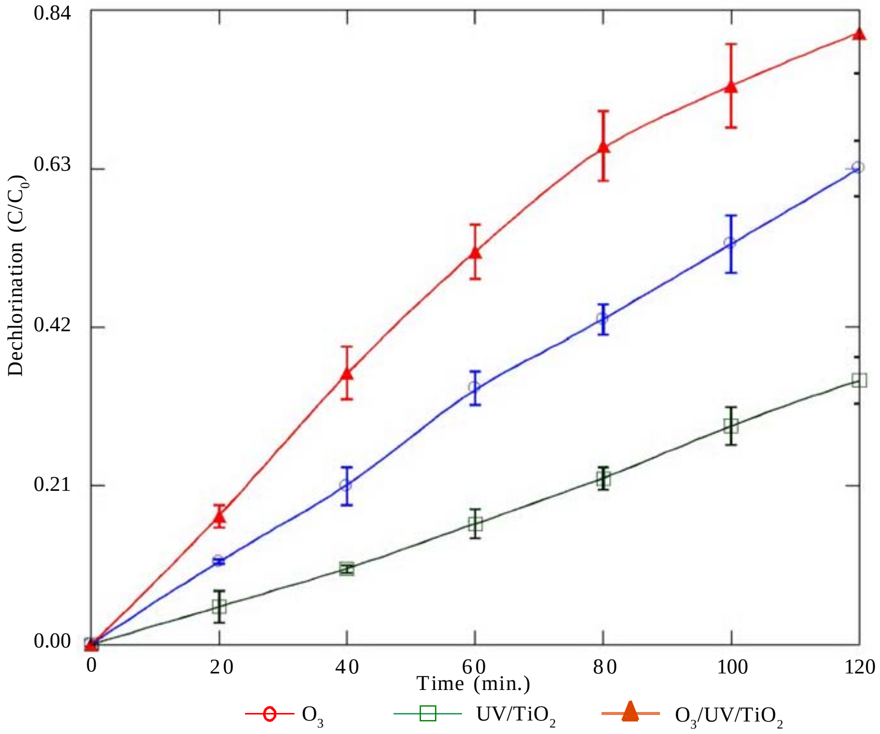

Fig. 8: Relative chloride ion concentration profiles during 2, 4-D mineralization

O_3/UV/TiO_2 was the most efficient. Dechlorination values for the O_3, UV/TiO_2 and O_3/UV/TiO_2 processes at the end of the 2 h. experiments were about 35, 63 and 81%, respectively. The average dechlorinations during the experiments in O_3/UV/TiO_2 and O_3 were about three and two folds the value for the UV/TiO_2 process, respectively. But, with respect to the values in UV/TiO_2, the dechlorination ratios in O_3 and O_3/UV/TiO_2 started to decline from 80 min. and continued to the end. Since the detected aliphatic intermediates were carboxylic acids, presumably only the aromatic intermediates were chlorinated. The smallest dechlorinations in UV/TiO_2 can be attributed to a very slow 2, 4-D decay and formation of 2, 4-DCP, which was the only aromatic intermediate and considered to be more resistant to degradation than 2, 4-D. The enhanced dechlorination in O_3, despite the selective reaction of ozone with organic compounds, may be attributed to relatively large ozone supply rate ($\approx$ 2.0 mg/L/min.). The two apparently major unidentified aromatics (RT $\approx$ 4.5 min. and 6.6 min.) in the O_3 process (Fig. 4) could be chlorinated in addition to 2, 4-DCP. The relatively slow 2, 4-D decay and the formation of possibly chlorinated aromatics in significant amounts in O_3 resulted in smaller dechlorinations compared to the values in O_3/UV/TiO_2. Detection the aromatic intermediates, including 2, 4-DCP, only for a short period and at very low concentrations, exhibited that dechlorination was presumably the first and/or major step in the O_3/UV/TiO_2 process. The largest dechlorination values in O_3/UV/TiO_2 can obviously be attributed to a large number of $^{\cdot}$OH generation, its high oxidation potential and non-selective reactions with 2, 4-D and its chlorinated aromatic intermediates. Despite complete disappearance of 2, 4-D and its aromatic intermediates, the dechlorination values were less than 90% in the O_3/UV/TiO_2 process by the end of the experiments. Reaction between chloride ions and $^{\cdot}$OH resulting in the reduced chloride concentrations may be ruled out in this case because the reaction is considered to be significant at high ($\geq$ 0.1 M) chloride concentrations only (Kiwi, *et al.*, 2000). The dechlorination values could have been underestimated, since the background chloride concentrations (before oxidation), which varied between 5% and 7%, were taken as zero in all of the experiments. The relatively larger background chloride concentrations may be the result of agitation of 2, 4-D solution due to mixing (all experiments) and air flow (experiments involving O_3) before commencing the experiments.

In aqueous solution, mineralization of low concentration 2, 4-D ($\approx$ 45 μM) by the O_3, UV/TiO_2 and O_3/UV/TiO_2 processes was investigated, using the world's first high-strength fiber catalyst. 2, 4-D degradation and TOC removal followed pseudo first-order reaction kinetic while the mineralization was greatly enhanced in O_3/UV/TiO_2. The removal rates for 2, 4-D and TOC in O_3/UV/TiO_2 were about 1.5 and 2.4-folds larger than the summation of the corresponding values for O_3 and UV/TiO_2. The O_3/UV/TiO_2 process was characterized by a few aromatic intermediates and their short lives, fast degradations of the aliphatic intermediates despite their presence in a relatively larger number and dechlorination as a major step in the mineralization. The enhanced dechlorination and 2, 4-D mineralization in the O_3/UV/TiO_2 process were due to the increased ozone decomposition and the reduced electron-hole recombination on TiO_2 surface resulting in a large number of $^{\cdot}$OH generation. The results exhibited that photocatalytic ozonation with TiO_2 fiber catalyst is very promising to overcome the problems being faced in AOP using TiO_2 as a photocatalyst: separation of catalyst in suspension and reduced efficiency of immobilized catalyst (e.g. TiO_2 film/fiber).

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