Heterogeneous photocatalytic ozonation of 2,4-D in dilute aqueous solution with TiO2 fiber

R. R. Giri, H. Ozaki, R. Takanami and S. Taniguchi

ABSTRACT

Photocatalytic ozonation (O3/UV/TiO2) is an emerging oxidation method for recalcitrant organic contaminants in water. However, immobilised TiO2 catalysts suffer from reduced photonic efficiency. Therefore, TiO2 catalysts with excellent mechanical and thermal properties and enhanced photonic efficiencies are sought. This paper aimed to elucidate the mineralisation of low concentration 2,4-D (45.0 μM) by O3/UV/TiO2 using the world’s first high-strength TiO2 fibre in laboratory batch experiments. 2,4-D degradation and TOC removal followed pseudo first-order reaction kinetic. The removal rates for 2,4-D and TOC in O3/UV/TiO2 were 1.5 and 2.4-fold larger than the summation of the values for ozonation (O3) and photocatalysis (UV/TiO2), respectively. O3/UV/TiO2 was characterised by few aromatic intermediates with low abundance, fast degradations of aliphatic intermediates and dechlorination as a major step. The significantly enhanced 2,4-D mineralisation in O3/UV/TiO2 was attributed to increased ozone dissolution and decomposition, and reduced electron–hole recombination resulting in large number of hydroxyl radical (OH) formation from more than one parallel path. The discrepancies in the organic carbon mass budget were attributed to few apparently major unidentified intermediates, while chlorine mass balance was reasonably acceptable. The mineralisation efficiency of O3/UV/TiO2 with the TiO2 fibre can further be enhanced by optimisation of experimental design parameters. The new TiO2 fibre is very promising to overcome the problem of reduced efficiency of TiO2 catalyst in an immobilised state.

Key words | dechlorination, hydroxyl radical, intermediates, mass budget, rate constant, TOC

INTRODUCTION

The ever increasing production and use of chlorinated organic chemicals resulting in their widespread detection in the water environment and stringent regulations being adopted, especially in industrialised countries, are demanding more efficient treatment methods. Photocatalysis with TiO2 and UV irradiation (UV/TiO2) and ozonation (O3) are two commonly used advanced oxidation processes (AOP) in water and wastewater treatment. However, UV/TiO2 is a very slow process resulting in often more toxic and persistent byproducts (Peller et al. 2003, 2004; Beltran et al. 2005; Terashima et al. 2006), while O3 is inefficient due to selective reaction of ozone with organics at acidic and neutral pH (Brillas et al. 2003, 2004; Agustina et al. 2005; Li et al. 2005). Photocatalytic ozonation with TiO2 in the presence of UV irradiation (O3/UV/TiO2) is an emerging and promising oxidation method (Agustina et al. 2005; Beltran et al. 2005; Giri et al. 2007).

Titanium dioxide (TiO2) powder is a common photocatalyst in TiO2-assisted AOP. Despite its high photonic efficiency, the separation of TiO2 powder in aqueous suspension has been a major difficulty. Though the recent development of TiO2 film and fibre catalysts is a very important step forward to overcome this difficulty, the immobilised catalysts suffer with reduced photonic efficiency. Therefore, immobilised TiO2 catalysts with larger photonic efficiency are needed for enhanced mineralisation.
of recalcitrant organic pollutants in low aqueous solutions. TiO$_2$ fibre catalysts can be superior to film catalysts, as the latter can not provide sufficient contact area to micro-pollutants resulting in their smaller removal efficiencies.

The characteristics of a TiO$_2$ fibre catalyst are important factors influencing photonic efficiency and hence the mineralisation of organics in a heterogeneous photocatalytic ozonation process. Ube Industries Ltd., Japan, has recently developed the world’s first high-strength TiO$_2$ fibre catalyst. It is a continuous white-coloured fibre with a small diameter (8.0 $\mu$m) and the surface is densely covered with nanoscale anatase-TiO$_2$ crystals (8.0 nm). The tensile strength of the fibre measured by the single filament method is 2.5 GPa, which is significantly larger than those of the existing TiO$_2$ fibres (<1.0 GPa). Details on this TiO$_2$ fibre catalyst can be found elsewhere (Ishikawa 2004). This paper aims to characterise the mineralisation of 2,4-dichlorophenoxyacetic acid (2,4-D) in low aqueous solutions (45.0 mM) by the O$_3$/UV/TiO$_2$ process using the newly developed TiO$_2$ fibre catalyst, and compares the results with those of O$_3$, TiO$_2$-catalysed ozonation (O$_3$/TiO$_2$) and UV/TiO$_2$ in laboratory batch experiments.

**MATERIALS AND METHODS**

**Materials**

2,4-D standard (Cica-Reagent) was obtained from Kanto Chemical Co., Inc. A Pyrex glass reactor (8.0 L capacity, ID: 18.4 cm, h: 30 cm) with a 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$_2$ fibre catalyst (20 cm $\times$ 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 $\times$ 3 mm opening). Details on reagents, ozone generation, UV irradiation and disposal of gas phase residual ozone are given elsewhere (Giri et al. 2007).

**Experimental**

Seven and half litres of 45.0 $\mu$M 2,4-D solution without initial pH adjustment was poured into the reactor. The catalyst module was placed inside the reactor in UV/TiO$_2$ and O$_3$/UV/TiO$_2$ experiments. The ozone generator, carrier gas flow metre, ozone concentration monitoring device, reactor, pump and absorption tower were connected in series as illustrated in Figure 1. The solution was continuously mixed ($\approx$ 300 rpm), samples were taken at 20 min interval for analysis, while the experiments were carried out for a period of 2 hours. The carrier gas flow rate and ozone concentration in it were maintained at 1.0 L/min and 2.0 mg/L, respectively, throughout the experiments in O$_3$ and O$_3$/UV/TiO$_2$ processes. Other details on the experimental procedure are given elsewhere (Giri et al. 2007).

**Analyses**

The samples were analysed for remaining 2,4-D and intermediate byproducts using HPLC with UV detector (Model: D-7000, Hitachi, Japan). Both 2,4-D and its aromatic intermediates were analysed as described elsewhere (Giri et al. 2007). Supelcogel C-610H (30 cm $\times$ 7.8 mm ID $\times$ 9 $\mu$m) together with Supelguard C-610H (5 cm $\times$ 4.6 mm ID) columns with 30°C oven temperature, 20 $\mu$L sample volume and 0.1% H$_3$PO$_4$ 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 oxidised 2,4-D samples with the peaks of various known standards. Total organic carbon (TOC), residual dissolved ozone and free chloride ion concentrations were measured as described earlier (Giri et al. 2007). Organic chlorine contents of the samples were measured using a total organic halogen analyser (Model: TOX-100, Mitsubishi Chemical Corporation, Japan) coupled with an adsorption module (Model: TXA-03, two columns adsorption method).

**RESULTS AND DISCUSSION**

2,4-D degradation and rate constant

The experiments were carried out in triplicate and average values are presented in figures with the error bars indicating standard deviations. The initial average pH values of 2,4-D solutions ($\approx$ 45 $\mu$M) for O$_3$, UV/TiO$_2$, O$_3$/TiO$_2$ and O$_3$/UV/TiO$_2$ were 4.36, 4.32, 4.35 and 4.33, respectively,
which gradually decreased during 2-hours oxidation. Relative concentration profiles (Figure 2) demonstrated effectiveness of the four processes to degrade 2,4-D. The half-life periods of 2,4-D in the systems with the order mentioned above were approximately 60, 110, 56 and 29 min, respectively. Approximately 83, 54 and 90% 2,4-D was degraded in O₃, UV/TiO₂ and O₃/TiO₂ at the end of 2-hours oxidation, while 100% degradation was achieved in less than 2 hours in O₃/UV/TiO₂.

2,4-D oxidations in the four processes were well described by pseudo first-order reaction kinetic (Table 1). The degradation rate values ($k$) for O₃, O₃/TiO₂ and O₃/UV/TiO₂ were approximately 2.3, 2.9 and 4.9 times of the value for UV/TiO₂. The $k$ value for O₃/UV/TiO₂ was 1.5 times of the summation of the values for O₃ and UV/TiO₂ systems. Similarly, it was 1.2 times of the summation of the values for UV/TiO₂ and O₃/TiO₂. Though the $k$-value for UV/TiO₂ in this investigation is similar to that reported

Figure 1 | A schematic diagram of experimental setup.

Figure 2 | Relative concentration profiles of 2,4-D.
earlier with TiO₂ powder (Giri et al. 2007), the value for O₃/UV/TiO₂ with the TiO₂ fibre is relatively smaller, which can be attributed to larger reaction volume (7.5 L) than used in the earlier investigation (1.2 L) with similar ozone supplies per minute. Therefore, it is possible to further enhance 2,4-D degradation efficiency by O₃/UV/TiO₂ system with the TiO₂ fibre by optimising experimental design parameters including ozone supply rate. It is evident from the results that O₃/UV/TiO₂ with the new TiO₂ fibre can be a very promising method for efficient degradation of organic pollutants and to overcome the major problem of separating TiO₂ powder in suspension.

Although a hydroxyl radical (OH) possesses the second highest oxidation potential after a positively charged hole (Equation 1) on TiO₂ surface (Munter 2001) and is considered as the sole oxidising species, 2,4-D decay in UV/TiO₂ was very slow, presumably due to recombination of the electrons and positive holes (Farre et al. 2005). Since the oxidation took place under acidic pH conditions, the formation of OH due to ozone decomposition can be ruled out in O₃ (Beltran et al. 2005). The enhanced 2,4-D decay in O₃ may be attributed to relatively larger ozone supply (2.0 mg ozone per minute). Further enhanced 2,4-D decay in O₃/TiO₂ with the same ozone inflow indicated additional decay other than by direct ozonation. One proposed mechanism for catalytic ozonation assumes that catalyst promotes ozone dissolution and initiates its decomposition (Yang et al. 2007 cited Cooper & Burch 1999). Surface reaction of ozone with Ti(III) sites produces ozonide ion radical (Equations 2 and 3) (Beltran et al. 2005), which ultimately results in OH. The larger residual dissolved ozone concentrations for O₃/TiO₂ (Figure 2) can be attributed to increased ozone dissolution in the presence of TiO₂. Further ozone decomposition takes place in presence of UV irradiation (Piera et al. 2000; Farre et al. 2005) according to Equations 4–6. The smallest and almost unchanged residual dissolved ozone concentrations for O₃/UV/TiO₂ (Figure 3) are consistent with the argument. Thus, more than one parallel path for OH formation is available in O₃/UV/TiO₂ resulting in the highest 2,4-D decaying efficiency.

\[
\text{TiO}_2 + \text{hv} \rightarrow \text{e}^- + \text{h}^+ 
\]

(1)

\[
\text{Ti}^{\text{IV}} + \text{e}^- \rightarrow \text{Ti}^{\text{III}} 
\]

(2)

\[
\text{Ti}^{\text{III}} - \text{O}_3^- \rightarrow \text{Ti}^{\text{IV}} + \text{O}_3^- 
\]

(3)

\[
\text{O}_3 + \text{H}_2\text{O} + \text{hv} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 
\]

(4)

\[
\text{H}_2\text{O}_2 \rightarrow \text{HO}_2^- + \text{H}^+ 
\]

(5)

\[
\text{O}_3 + \text{HO}_2^- \rightarrow \text{O}_3^- + \text{HO}_2 
\]

(6)

\[
\text{O}_3 + \text{e}^- \rightarrow \text{O}_3^- 
\]

(7)

\[
\text{O}_3^- + \text{H}^+ \rightarrow \text{HO}_3^- \rightarrow \text{OH} + \text{O}_2 
\]

(8)

### Formation of intermediates

Though only aromatic intermediates of 2,4-D oxidation were reported in our earlier investigation (Giri et al. 2007), attempts are made to identify all the detected aliphatic and aromatic 2,4-D intermediate species in the present work.

### Table 1

<table>
<thead>
<tr>
<th>Oxidation system</th>
<th>2,4-D degradation k (1/hr)</th>
<th>TOC removal k (1/hr)</th>
<th>R²</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₃</td>
<td>0.89</td>
<td>0.09</td>
<td>0.981</td>
<td>0.997</td>
</tr>
<tr>
<td>UV/TiO₂</td>
<td>0.39</td>
<td>0.14</td>
<td>0.998</td>
<td>0.972</td>
</tr>
<tr>
<td>O₃/TiO₂</td>
<td>1.15</td>
<td>0.21</td>
<td>0.963</td>
<td>0.983</td>
</tr>
<tr>
<td>O₃/UV/TiO₂</td>
<td>1.93</td>
<td>0.56</td>
<td>0.988</td>
<td>0.988</td>
</tr>
</tbody>
</table>

Figure 3 | Dissolved residual ozone concentrations.
aromatic byproducts to understand possible degradation pathways for 2,4-D in this paper. Despite very slow 2,4-D oxidation, the least number of intermediates were detected in UV/TiO2. 2,4-dichlorophenol (2,4-DCP) was the major aromatic intermediate, while benzyl alcohol was also detected at low concentrations towards the end of the experiments. Maleic acid and an unknown were aliphatic intermediates detected in UV/TiO2. Ozonation was characterised by the largest number of intermediates including eight aromatics (2,4-DCP, benzyl alcohol and six unknowns) and ten aliphatics (oxalic acid, maleic acid, glyoxylic acid, glycolic acid and six unknowns). Two unknown aromatics (RT < 6.6 and 4.5 min) and two aliphatics (oxalic acid and glyoxylic acid) appeared as major intermediates in O3. Though only two aromatics (unidentified) were present in O3/TiO2, the number and type of identified aliphatics (a total of eleven) were similar to those in O3, while oxalic acid and an unknown were apparently two major aliphatics.

Three aromatics (2,4-DCP, benzyl alcohol and an unknown) and nine aliphatics (Figure 4) were detected in O3/UV/TiO2. Unlike in O3, UV/TiO2 and O3/TiO2, the aromatic intermediates were detected only in the middle of the experiments and at low concentrations, while abundance of the detected aliphatics reached peak values and decreased significantly by the end of the experiments in O3/UV/TiO2, indicating enhanced 2,4-D mineralisation.

Though many aliphatics were not identified, carboxylic acids appeared to be stable end products of 2,4-D oxidation in O3, and O3/TiO2, while 2,4-DCP was more resistant to degradation than the parent compound in UV/TiO2. The larger number of intermediates in oxidations involving ozonation can be attributed to selective ozone reaction at acidic pH conditions resulting in formation of saturated carboxylic acids as end products (Agustina et al. 2005). A large abundance of oxalic acid, which is a typical refractory compound to conventional treatments (Beltran et al. 2002), in O3 and O3/TiO2 during 2,4-D oxidations also exhibited the fact. Very small abundances of oxalic acid in O3/UV/TiO2 (Figure 4) once again indicated efficient 2,4-D mineralisation by the process.

TOC removal, rate constant and mass budget

Unlike 2,4-D oxidations, no significant difference in TOC removals were observed between O3 and UV/TiO2 until the first-half of the experiments (Figure 5). The UV/TiO2 then appeared to be more efficient than O3, and the difference between them gradually increased until the end. Similar to 2,4-D degradations, O3/TiO2 was more efficient than O3 and UV/TiO2, while O3/UV/TiO2 was the most efficient among the four processes studied in terms of TOC removal. The TOC removals by O3, UV/TiO2, O3/TiO2 and O3/UV/TiO2 at the end of 2-hour experiments were 17, 23, 33 and 67%, respectively.

TOC removals by the processes were well described by pseudo first-order reaction kinetic (Table 1). The smaller TOC removal rate (k) values compared to those for 2,4-D oxidations were obvious. The k values for UV/TiO2, O3/TiO2 and
O₃/UV/TiO₂ were approximately 1.5, 2.3 and 6.2-fold larger than the value for O₃. The k value for O₃/UV/TiO₂ was approximately 2.4 and 1.6-fold larger than the summation of the values for O₃ and UV/TiO₂, and UV/TiO₂ and O₃/TiO₂ respectively, which showed significantly enhanced TOC removal efficiency of O₃/UV/TiO₂. Though the TOC removal rate by O₃/UV/TiO₂ in this investigation is slightly smaller than the value reported earlier with TiO₂ powder (Giri et al. 2007), the removal efficiency with the TiO₂ fibre can be further enhanced by optimising experimental parameters.

Dissolved ozone can easily accept electrons produced on TiO₂ surface (Equation 7) reducing the possibility of their recombination with positive holes (Beltran et al. 2005). A large amount of hydrogen peroxide and hence OH can also be produced from dissolved ozone in the presence of UV irradiation according to Equations 4–6 and 8. Though ozone photolysis is a slow process in the beginning, it is considered as an important source of OH after a few minutes. With a high extinction coefficient value for ozone at 254 nm wavelength (ε = 3300 M⁻¹ cm⁻¹), a large number of OH are generated from ozone photolysis (Munter 2001). Thus, three parallel paths of OH generation are available in O₃/UV/TiO₂ in addition to direct ozonation and photolysis of 2,4-D and its degradation intermediates. The smallest and almost unchanged residual dissolved ozone concentrations (Figure 2) can be taken as evidence of efficient ozone decomposition in the process.

The mass balance for organic carbon was checked based on the identified byproducts of 2,4-D degradation and measured TOC values during 2-hour oxidation in O₃/UV/TiO₂ (Figure 5). The mass balance could not be presented in our earlier report (Giri et al. 2007), because only aromatic intermediates were measured and identified. Glyoxylic acid had the largest contribution to the mass budget, while those of 2,4-DCP and formic acid were relatively smaller (Figure 6) among the identified intermediates. Closing errors between summation of organic carbon contents in the byproducts including 2,4-D and the measured TOC values were reasonably small until 40 min. However, the errors afterwards continued to increase until the end of the experiments. Two unidentified aliphatics (RT = 15.25 and 14.33 min) appeared as major byproducts in terms of their abundance (Figure 4), and remained in solution in considerable amounts until the end. The small errors in the first half of the experiments may be the result of a larger contribution of glyoxylic acid, while the large errors in the second half can be attributed to a reduced contribution of glyoxylic acid, presence of the two unknown aliphatics in considerable amounts and possibly several undetected intermediates at low concentrations.

**Dechlorination and mass budget**

Chlorine content in chlorinated hazardous organics is considered as a measure of their toxicity, and therefore dechlorination has significance in degradation of the organics. Dechlorination in a sample was calculated as the ratio of measured free chloride ion concentration to theoretical chlorine content in the sample before oxidation. The dechlorination profiles (Figure 7) were similar to relative 2,4-D concentration profiles (Figure 2). The dechlorination values for UV/TiO₂, O₃, O₃/TiO₂ and O₃/UV/TiO₂ at the end of two-hour long experiments were approximately 35, 63, 77 and 81%, respectively. Average dechlorinations in O₃, O₃/TiO₂ and O₃/UV/TiO₂ during the experiments were approximately 2.0, 2.7 and 3.0-fold of the values for UV/TiO₂. Moreover, the values gradually declined in the latter part of the experiments. Despite similar dechlorinations for the UV/TiO₂ system with TiO₂ powder reported earlier (Giri et al. 2007) and fibre catalyst, the values for O₃ and O₃/UV/TiO₂ in this investigation are relatively smaller, presumably due to the larger reaction volume.

Only the aromatic intermediates of 2,4-D oxidation were presumably chlorinated since the aliphatics were
carboxylic acids. A detailed insight of dechlorination steps was difficult as many of the detected aromatics were not identified. The smallest dechlorinations in UV/TiO₂ were mainly attributed to the formation of 2,4-DCP and slow decay of both 2,4-D and 2,4-DCP. The increased dechlorinations in O₃ were presumably due to enhanced oxidation of the aromatics including 2,4-DCP. However, two apparently major unidentified aromatics could have resulted in smaller dechlorinations in O₃ than in O₃/TiO₂ and O₃/UV/TiO₂. The larger dechlorinations in O₃/TiO₂ may be attributed to a small number of aromatics and a significant decrease of their abundance by the end of the experiments. The largest dechlorinations in O₃/UV/TiO₂ were attributed to the complete disappearance of the detected aromatic intermediates by the end of the experiments. However, the dechlorination values in O₃/UV/TiO₂ were less than 90%. The use of chloride ions for OH scavenging was ruled out in these experiments as the reaction is significant only when the chloride concentrations are more than 0.10 M (Kiwi et al. 2000). Actual dechlorinations could have been underestimated in these experiments as chloride concentrations in the samples before oxidation were significant (5–7% of the values at the end of the experiments), which were taken as zero (i.e. chloride concentration of a sample after oxidation was calculated by subtracting the value before oxidation). The relatively larger background chloride concentrations before oxidation could be the result of agitation due to mixing and air flow.

A separate set of experiments for 2,4-D degradation by O₃/UV/TiO₂ was carried out for chlorine mass balance. Organic chlorine contents in the oxidised 2,4-D solutions were also measured, possibly for the first time, in addition to free chloride ion contents, and the mass balance is illustrated in Figure 8. The organic, inorganic and total chlorine mass at 40, 80 and 120 min were approximately 48, 18, 8; 42, 73, 87 and 90, 92, 95% respectively. Despite the complete disappearance of 2,4-D and its aromatic byproducts in HPLC analysis, approximately 8% organic chlorine was remaining at the end of the experiments. Most probably, 2,4-D and its chlorinated aromatic intermediates were present at low concentrations, which could not be detected in HPLC measurements, resulting in the presence of organic chlorine in considerable amounts at the end. The chlorine mass budgets at 40 min intervals were fairly good with closing errors ranging from 5 to 10%. The relatively larger closing errors in these experiments also may be attributed to underestimation of free chloride ions as discussed previously. The background free chloride contents before 2,4-D oxidation (5–7%) were similar to the closing errors in chlorine mass budgets (5–10%), which may indicate an underestimation of free chloride ions.

Degradation of 2,4-D with hydroxyl radical

The results and discussion presented so far showed that OH was abundant and presumably the major oxidant for 2,4-D
mineralisation in O$_3$/UV/TiO$_2$. Some reaction pathways for 2,4-D with $^\cdot$OH are suggested based on the information obtained in this investigation.

2,4-D is highly susceptible to attack by $^\cdot$OH (Peller et al. 2004), while hydrogen abstraction, $^\cdot$OH addition and electron transfer are prominent degradation mechanisms (Peller et al. 2003; Peller & Kamat 2005). The proposed reaction pathways are illustrated in Figure 9. $^\cdot$OH gets an electron from electron-rich oxygen of 2,4-D molecule, which is the initiation of radical reaction. As a result, C$_1$(O bond is cleaved resulting in 2,4-dichlorophenoxide ion and ethanoic acid radical (Figure 9(a)). The phenoxide ion after protonation changes to 2,4-DCP, while one succinic acid molecule is formed from two ethanoic acid radicals. Maleic and fumaric acids are formed by abstraction of two hydrogen atoms in succinic acid (Figure 9(c) and (d)).

On the other hand, $^\cdot$OH addition to ethanoic acid radical results in glycolic acid, while abstraction of two hydrogen atoms in glycolic acid produces glyoxylic acid (Figure 9(e)). Moreover, abstraction of one hydrogen atom from glyoxylic acid followed by $^\cdot$OH addition reaction results in oxalic acid, which is very resistant to degradation. However, reaction of oxalic acid with $^\cdot$OH may result in formic acid in limited amounts as suggested by the identified aliphatic byproducts of 2,4-D oxidation. Though maleic and fumaric acids were generated from succinic acid by hydrogen abstraction in the suggested reactions, the latter was not detected in the experiments, possibly due to its very weak absorption in the UV region.
fast reaction with OH. An extremely large abundance of maleic acid rather than that of fumaric acid may indicate abstraction of two similar hydrogen atoms from succinic acid (Figure 9(c)), being a favourable reaction.

Since OH addition to substituted carbon atoms of 2,4-DCP is more favourable to nonsubstituted ones (Peller et al. 2003; Peller & Kamat 2005) and dechlorination was a major step in 2,4-D mineralisation, removal of chlorine atoms from 2,4-DCP was probably the first step in its oxidation with OH. Then, the non-chlorinated phenoxide ion is reported to react with OH exclusively forming phenoxy radical (Peller & Kamat 2005). However, further decomposition of the intermediates of 2,4-DCP oxidation is not well understood. Moreover, there could be other major/minor reaction pathways in addition to the suggested ones, because many detected intermediates were not identified.

CONCLUSIONS

Photocatalytic ozonation with the newly developed TiO2 fibre catalyst was very efficient to mineralise low concentrations of 2,4-D in water. 2,4-D degradation and TOC removals followed pseudo first-order reaction kinetic. The removal rates for 2,4-D and TOC in O3/UV/TiO2 were 1.5 and 2.4-fold larger than the summation of the values in O3 and UV/TiO2, respectively. The O3/UV/TiO2 process was characterised by few aromatic intermediates with low abundance, fast degradations of the aliphatic intermediates despite their relatively large number and dechlorination as a major step. The significantly enhanced 2,4-D mineralisation in O3/UV/TiO2 were due to increased ozone dissolution and decomposition, and to reduced electron–hole recombination in the presence of TiO2 resulting in large amounts of OH formation from more than one parallel path. The large discrepancies in organic carbon mass budget in the latter part of 2,4-D oxidation were mainly due to a few apparently major unidentified intermediates, while the chlorine mass budget was reasonably acceptable. The results exhibited that the newly developed TiO2 fibre catalyst is very promising to overcome two major problems in TiO2-catalysed advanced oxidation processes: separation of TiO2 powder suspension in water and reduced efficiency of TiO2 in its immobilised state.

REFERENCES


