Photocatalytic oxidation of low concentration 2,4-D solution with new TiO$_2$ fiber catalyst in a continuous flow reactor

Y. Terashima*, H. Ozaki**, R.R. Giri***, T. Tano****, S. Nakatsuji** and R. Takanami** and S. Taniguchi***

*Dept. of Human Environment, Osaka Sangyo University, 3-1-1 Nakataito, Daito City, 574-8530 Osaka, Japan (E-mail: *terashima@due.osaka-sandai.ac.jp*)

**Dept. of Civil Engineering, Osaka Sangyo University, 3-1-1 Nakagaito, Daito City, 574-8530, Japan (E-mail: *ozaki@ce.osaka-sandai.ac.jp*)

***New Industrial R & D Center, Osaka Sangyo University, 3-1-1 Nakataito, Daito City, 574-8530 Osaka, Japan (E-mail: *sn04001@sub.osaka-sandai.ac.jp*)

****Ube Industries Ltd., Oaza-Ogushi, Ube City, 755-8633 Yamaguchi, Japan (E-mail: *27021u@ube-ind.co.jp*)

Abstract Environmental pollution by low concentrations of 2,4-Dichlorophenoxyacetic acid (2,4-D) is a concern these days due to ever increasingly stringent regulations. Photocatalysis with immobilized TiO$_2$ fiber is a promising oxidation method. Laboratory experiments on photocatalytic degradation of 0.045 mmol l^{-1} 2,4-D with the world's first high-strength TiO$_2$ fiber catalyst were carried out in a continuous flow reactor in which the degradations were, in general, similar to those with high 2,4-D concentrations investigated elsewhere. Degradation and mineralization of 2,4-D were significantly enhanced with no initial pH adjustments. The rate constants for total organic carbon (TOC) without pH adjustment were about two-fold bigger than the pH adjustment cases. CO$_2$ gas measurement and carbon mass-balance were carried out for the first time, where about 34% organic carbon converted into CO$_2$ gas during four-hour oxidation. 2,4-Dichlorophenol (2,4-DCP), phenol, benzyl alcohol and two unknowns (RT $\approx$ 2.65 and 3.78 min.) were detected as aromatic intermediates while Phenol was the new aromatic in HPLC analysis. Dechlorination efficiencies were high ($>$70%) in all the cases, and more than 90% efficiencies were observed in chloride mass balance. Bigger flow rates and solution temperature fixed at 20 °C without pH adjustment greatly enhanced 2,4-D mineralization. These results can be an important basis in applying the treatment method for dioxin-contaminated water and wastewater.

Keywords 2,4-dichlorophenoxyacetic acid; dechlorination; mass balance; photocatalysis; rate constant; total organic carbon

Introduction

Photocatalysis is emerging as a promising technology for oxidative degradation of hazardous and recalcitrant pollutants in water environment. TiO$_2$ is the most commonly used semiconductor in photocatalysis. Although TiO$_2$ powder is very effective in heterogeneous photocatalysis due to its good contact with UV light and relatively high quantum yield, its complete separation from the water environment requires expensive techniques such as membrane filtration, which is a major disadvantage (Modestov and Lev, 1998; Geissen *et al.*, 2001; Li *et al.*, 2003). This is overcome by using immobilized TiO$_2$ photocatalyst although its contact with UV light and quantum yield are relatively small. Mechanical and thermal properties of immobilized TiO$_2$ photocatalyst are of concern for its continuous and effective use (Li *et al.*, 2003). Several types of TiO$_2$ photocatalytic fibers have been developed for effective degradation of environmental pollutants. Ube Industries Ltd., Japan has recently developed the world's first high-strength photocatalyst

(TiO$_2$-covered SiO$_2$ fiber) with excellent mechanical and thermal properties (Ishikawa, 2004), which is expected to be very effective for complete mineralization of hazardous pollutants (e.g. dioxins).
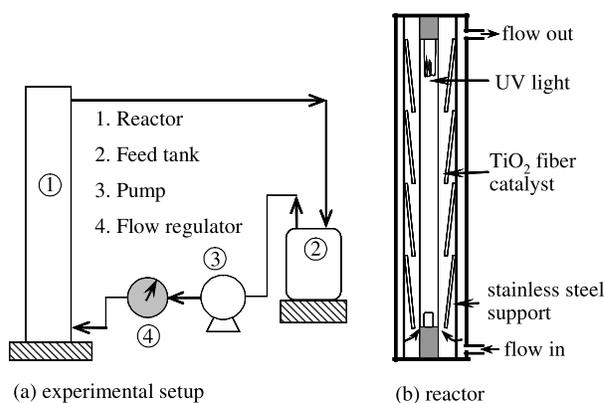
2,4-Dichlorophenoxyacetic acid (2,4-D) is possibly the most widely investigated herbicide for environmental pollution. It is used as a model contaminant for degradation of hazardous chemicals, for example: dioxins, in the water environment by advanced oxidation processes (AOP) like photocatalysis. Decomposition of very high 2,4-D concentrations (0.45 to 1.80 mmol l^{-1} in the water environment by photocatalysis and ozonation have been investigated (Djebbar and Sehili, 1998; Muller *et al.*, 1998; Piera *et al.*, 2000; Brillas *et al.*, 2003; Chu *et al.*, 2004; Drezewicz *et al.*, 2004; Singh and Muneer, 2004). However, 2,4-D pollution levels in the environment are significantly reduced due to advancement in treatments methods and ever increasingly stringent regulations. Since initial 2,4-D concentration and properties of TiO$_2$ catalyst significantly influence degradation kinetics and mineralization efficiency (Djebbar and Sehili, 1998; Modestov and Lev, 1998; Singh and Muneer, 2004), investigation on photocatalytic decomposition of 2,4-D at low concentration levels with the new TiO$_2$ catalyst is imperative.

This paper aimed to evaluate mineralization of low concentration 2,4-D (0.045 mmol l^{-1}) using the newly developed TiO$_2$ fiber photocatalyst module by Ube Industries Ltd. with UV light irradiation. Laboratory experiments were carried out at different temperatures, flow rates and initial solution pH in a continuous flow reactor. 2,4-D mineralization in terms of its degradation, total organic carbon (TOC) removal, formation of aromatic intermediates and dechlorination was evaluated. The results are expected to be a baseline in treating dioxin contaminated scrubber wastewater with this method.

Materials and methods

Materials

The experimental setup (Figure 1(a)) consists of a vertical continuous flow reactor (OD: 90 mm, h: 740 mm) made of non-corrosive steel, high-strength TiO$_2$ hollow fiber module catalyst, UV lamp, feed tank, flow-meter and pump (provided by Ube Industries Ltd., Japan). The UV tube lamp (254 nm, 10 mW/cm^2) is encased within the fiber module catalyst, which is then placed inside the reactor. The module consists of four coaxially supported cup-shaped TiO$_2$ fiber catalysts (Figure 1(b)). The catalyst (total surface area: 164,171 mm^2, area effective to UV: 70,370 mm^2) in each cup is rigidly supported by non-corrosive steel net. A closed airtight vessel (OD: 180 mm, h: 355 mm) made of high

1. Reactor
2. Feed tank
3. Pump
4. Flow regulator

(a) experimental setup

(b) reactor

flow out
UV light
TiO$_2$ fiber catalyst
stainless steel support
flow in

Figure 1 Schematic of experimental setup and reactor

quality quartz was used as feed tank. High purity standards of the required chemicals were obtained from Wako Pure Chemicals Ltd., Japan. Initial pH of 2,4-D solutions was adjusted with H_2SO_4 and NaOH solutions. Solution temperature inside the feed tank was maintained using a temperature-controlled water bath and ice pieces to evaluate the temperature effect on 2,4-D mineralization.

Experimental

The pump and flow regulator were connected in series with the reactor and feed tank (Figure 1(a)). About 7 litres of 2,4-D solution (total 8.0 litres with $0.045 \, mmol \, l^{-1}$) was poured into the recirculation tank and remaining solution into the pump. All the openings of the feed tank were made airtight and pumping was started. Flow was adjusted and liquid sample was taken from the sampling port in the feed tank. UV light was switched on and a stop-watch was started immediately after the sampling. Liquid samples were taken at twenty-minute intervals. A separate set of experiments was conducted for organic carbon mass-balance. Gas samples were collected in high quality aluminium bags by raising the water level in the feed tank and then forcing helium gas flow. All the experiments were carried out with 5 l/min flow rate except in flow rate effect for four-hour duration.

Analysis

The liquid samples were analyzed for 2,4-D concentrations and aromatic intermediates using Hitachi D-7000 HPLC with UV detector (Inertsil ODS-3 column: 150 mm × 3 mmID × 5 μm; column oven temperature: 35 °C; 20 μL sample volume; CH_3CN:H_2O: $CH_3COOH = 50:49:1$ (v/v) mobile phase with 0.4 mL/min flow rate). LCMS-2010A, Shimazdu and LCMS/MS, Applied Biosystems, (liquid chromatographic conditions similar to those in HPLC analyses, and 3200 QTRAP, APCI scan mode for mass spectrometry) were also employed for byproduct identification. Total organic carbon (TOC_d) and total inorganic carbon (TIC_d) in liquid samples were measured with TOC analyzer-810 (SIEVER). Gas samples collected from the feed tank were analyzed for CO_2 using Simazdu Gas Chromatograph: GC-8A (SHINCARBON ST 50/80 mesh column: 2 m × 3 mmϕ; helium as carrier gas at 50 ml/min, 150 °C column oven temperature, 210 °C injector and detector temperatures, 100 mA TCD current). Total inorganic carbon in gas phase (TIC_g) was calculated from CO_2 in the gas sample. Chloride ion concentrations in liquid samples were measured using a Hitachi L-7000 ion chromatograph with conductivity detector (GL-IC-A25 column: 150 mm × 4.6 mm ID; 40 °C column oven temperature and $4.0 \, mmol \, l^{-1} \, Na_2CO_3$ mobile phase with 1.0 mL/min flow rate).

Results and discussion

2,4-D degradation characteristics

Solution pH of about $0.045 \, mmol \, l^{-1}$ 2,4-D prior to adjustment varied between 4.0 and 4.23. Initial pH greatly influenced 2,4-D degradation among the three cases (pH, flow rate and temperature) considered. 2,4-D solution pH initially in neutral and alkaline regions decreased drastically to about 5 within half an hour. But, it did not change significantly when the initial values were about 5 or less. 2,4-D degradation decreased with increasing pH (Figure 2), which was consistent with the previous investigation results (Muller *et al.*, 1998; Singh and Muneer, 2004). Hydroxyl radical is pointed out as the main oxidizing species (Mokrini *et al.*, 1998; Peller *et al.*, 2003) and photonic efficiency was found to decrease with increasing solution pH (Singh and Muneer, 2004) in photocatalytic oxidation. The decreased 2,4-D degradation at higher pH can be attributed to decreased photonic efficiency.
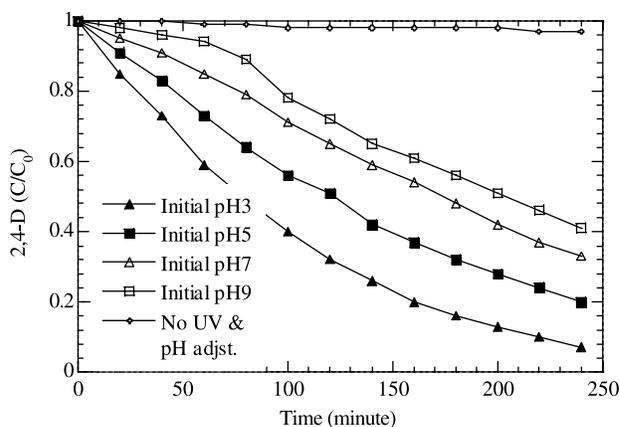
Figure 2 Degradation of 2,4-D with initial pH

2,4-D degraded completely in four-hours oxidation when solution pH was not adjusted. The degradation decreased with increasing temperature although the differences were not as significant as with initial pH cases. Lee *et al.* (2003) demonstrated great enhancement in 2,4-D degradation with increasing solution temperature in the Fe^{3+}/H_2O_2 system. Although OH radical is the main oxidizing species in the both cases, the reason behind faster 2,4-D degradation at lower temperature (20 °C in this investigation) is not well understood. Unlike with solution pH and temperature cases, 2,4-D degraded faster with bigger flow rates. However, the differences among the three flow rates were not as significant as with initial pH cases. The increased degradation with higher flow rates may be attributed to increased contact between OH radicals and 2,4-D molecules.

Degradations of 2,4-D in this investigation were best described by first-order kinetics. The degradation rate constant (k) values were significantly smaller with initial pH adjustment (except at pH3) than for the other two cases (Figure 3). But the initial pH highly influenced the rate constant. The value at pH 3 was 2.75 times the value at pH 9. Flow rate showed the second highest influence on k value. The value at 20 l/min flow rate was 1.4 times the value at 5 l/min Temperature showed the least influence on k among the three factors considered. The half-life periods of 2,4-D with pH adjustment cases varied
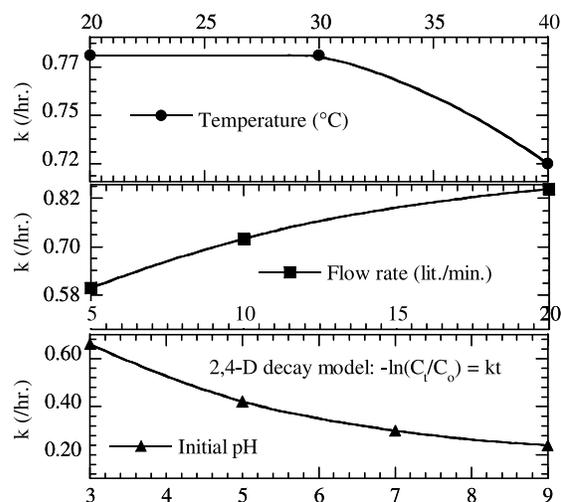
Figure 3 Variation of k with initial pH, Q and T

between 80 and 200 minutes, while the periods in other cases were about an hour. It appeared from the results that 2,4-D can be degraded most efficiently at 20 l/min flow rate and temperature fixed at 20 °C without pH adjustment among the cases considered in this investigation.

Formation of aromatic intermediates

Five aromatic intermediates were detected in HPLC analysis (Figure 4). Three of them (2,4-DCP, phenol and benzyl alcohol with retention time (RT) about 7.0, 3.45 and 2.98 min) were identified while the remaining two (RT ≈ 2.65 and 3.78 min) could not be confirmed. 2,4-DCP and benzyl alcohol as aromatic intermediates were consistent with the previous investigation results (Singh and Muneer, 2004) while Phenol has not yet been reported. The number of aromatic intermediates decreased with no pH adjustment cases. The three known and one unknown (RT ≈ 3.78 min) intermediates were detected with the three flow rates while only the three known intermediates were detected with fixed temperature cases. Only the three known ones were observed with 5 and 10 l/min flow rates while 2,4-DCP and Benzyl alcohol only were observed with temperature fixed at 20 °C.

Number and type of aromatic intermediates have great significance in complete mineralization of the model pollutant. 2,4-DCP was the major intermediate in all the cases considered (except with initial pH 9), which is more persistent and toxic than 2,4-D (Muller *et al.*, 1998). Phenol and benzyl alcohol were respectively the second and third most abundant intermediates with different flow rates while the order was reversed with fixed temperature cases. Abundance of the intermediates was not the same with different pH cases. A large number of intermediates may indicate longer and several degradation paths resulting in delayed mineralization of the model pollutant. Oxidation of 2,4-D without pH adjustment at 20 °C temperature and 20 l/min flow rate appeared to be more appropriate for smaller numbers of aromatic intermediates and hence fast degradation of 2,4-D.

Only 2,4-D and 2,4-DCP were detected in LCMS analysis. A preliminary LCMS/MS analysis of the liquid samples showed six aromatics including 2,4-D in which only 2,4-D and 2,4-DCP were identified. However, the mass spectra of the aromatic intermediates did indicate absence of chlorine except in 2,4-DCP. Acetophenone and 4-chlorophenol were suspected to be the two unknown intermediates. But, they could not be confirmed by HPLC and LCMS analyses. A close observation on the number, type and abundance of the aromatic intermediates may indicate more than one simultaneous degradation pathways for 2,4-D depending on experimental conditions. Two hypothetical 2,4-D
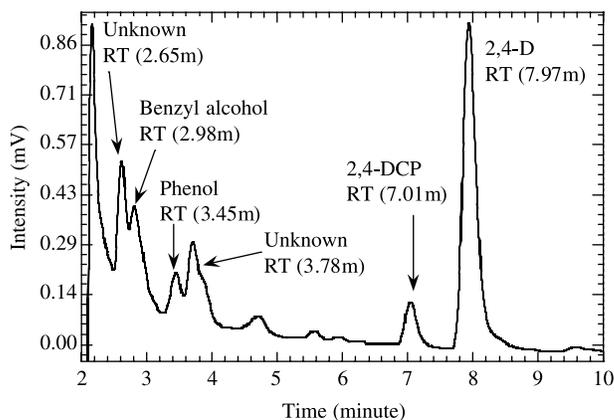

Figure 4 Aromatic intermediates in HPLC analysis

degradation pathways are suggested in Figure 5 based on the information obtained in this investigation. The first path appeared to be major since 2,4-DCP was the main aromatic intermediate in all the cases considered.

TOC removal and carbon mass balance

TOC is regarded as an indicator of complete mineralization of organic pollutants in oxidation processes. TOC removal with fixed initial pH cases were significantly smaller than in the other two cases possibly due to slow degradations and relatively larger numbers of intermediates. The removal varied between 23% and 40%. Slightly acidic and neutral initial pH exhibited higher TOC removals, which was consistent with 2,4-D degradation. TOC removal for the three flow rates and fixed temperatures without initial pH adjustment varied between 58% and 61%, and 61% and 65%, respectively. About 35% of the remaining TOC at the end of four-hour experiments without initial pH adjustment can be attributed to the presence of mainly aliphatic and some aromatic intermediates. Bigger flow rates and solution temperature fixed at 20 °C appeared more favourable from the TOC removal point of view also.

TOC removal rate constants were calculated assuming first-order kinetics for the three cases considered (Figure 6). Fixed temperature cases exhibited the highest removal rates. Although there were no significant differences in the rates with the three temperatures, 20 °C appeared favourable. The rate constant values for three flow rates were similar to those with the three fixed temperatures, but the value increased with flow rate. The values for initial pH adjustment cases were about half of those without adjustment. The removals were higher at neutral and slightly acidic conditions with adjustment in initial pH. TOC removal and the rate constant values were consistent with 2,4-D degradations.

Photon generation rate inside the reactor was calculated following Einstein's energy equation and the power of UV light. Photon utilization efficiency was calculated to be 23.3% based on the catalyst area effective to UV radiation. OH radical generation rate was 0.07 moles/hour assuming one photon produced one radical. Organic carbon removal rates in the reactor based on TOC removal and the OH radical generation rate for the different cases considered were consistent with the TOC removal rates (Figure 6).
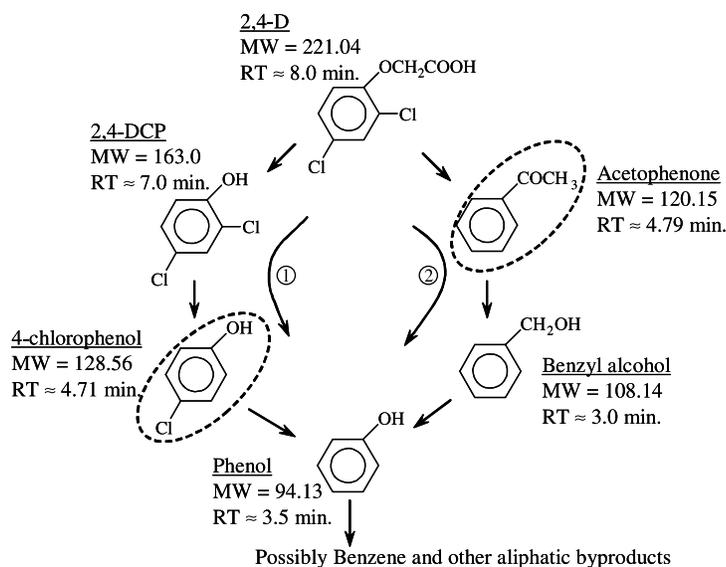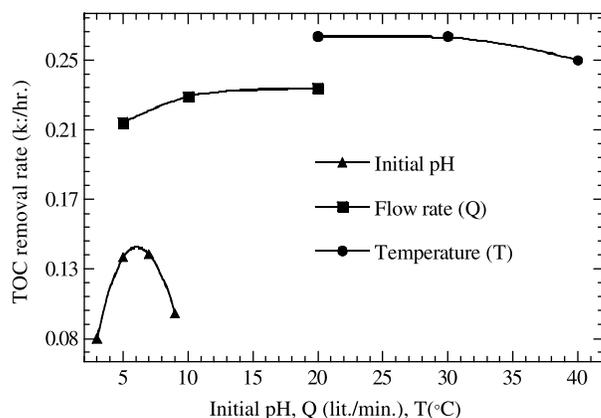

Figure 5 Suggested degradation pathways

Figure 6 TOC removal rate with pH, Q and T

The values varied between 0.375 and 0.961 mmol l^{-1} carbon per mole of OH radical per hour.

Carbon mass balance in terms of organic and inorganic components in 2,4-D oxidation with 5 l/min flow rate and without pH adjustment and temperature control is illustrated in Table 1. The closing errors in mass balance varied between 2% and 6%. Possibly one hundred per cent of the gases in the head space of the feed tank could not be collected with the method used resulting in 6% closing error. Gas phase inorganic carbon (TIC$_g$) at one-hour intervals were about 5%, 12%, 23% and 34% of the corresponding TOC values at zero minutes, which exhibited significance of CO$_2$ measurement in the mass balance.

Carbon mass balance in 2,4-D and the aromatic intermediates at one-hour intervals with no pH adjustment and solution temperature fixed at 20 °C is shown in Table 2. About 18% closing error (of the corresponding measured TOC) in mass balance at zero hours was due to the difference between the theoretical and measured TOC. Measured TOC values were always bigger than the theoretical ones due to several possible carbon

Table 1 Carbon mass balance in 2,4-D solution

Time (hour)	TOC$_d$ (m mol l^{-1})	TIC$_d$ (m mol l^{-1})	TIC$_g$ (m mol l^{-1})	TOC (m mol l^{-1})	Closing error m mol l^{-1} (%)	Initial 2,4-D (m mol l^{-1})
1	0.382	0.019	0.000	0.401	0.018	0.041
	0.327	0.036	0.020	0.383	(4.49)	
2	0.376	0.022	0.000	0.398	0.008	0.042
	0.287	0.055	0.048	0.390	(2.01)	
3	0.356	0.024	0.000	0.380	0.009	0.040
	0.230	0.054	0.087	0.371	(2.37)	
4	0.413	0.023	0.000	0.436	0.025	0.043
	0.206	0.059	0.146	0.411	(5.73)	

Table 2 Carbon mass balance (experiment at 20 °C)

Time (hour)	Carbon (m mol l^{-1}) in			Total (m mol l^{-1})	TOC (m mol l^{-1})	Closing error (%)
	2,4-D	2,4-DCP	Benzyl alcohol			
0	0.340	0.000	0.000	0.340	0.414	17.8
1	0.161	0.046	0.000	0.207	0.321	35.5
2	0.073	0.048	0.012	0.133	0.240	44.6
3	0.031	0.039	0.018	0.088	0.173	49.1
4	0.000	0.029	0.021	0.049	0.145	66.2

Table 3 Dechlorination in 2,4-D oxidation

Time (hour)	Initial 2,4-D (m mol l^{-1})	Theoretical chloride (m mol l^{-1})	Measured chloride (m mol l^{-1})	Dechlo-rination (%)
1	0.041	0.082	0.023	28.05
2	0.042	0.084	0.046	54.76
3	0.040	0.081	0.057	70.37
4	0.043	0.087	0.074	85.06

Table 4 Chlorine mass balance (experiment at 20 °C)

Time (hour)	Chlorine (m mol l^{-1})		Measured (m mol l^{-1})	Total (m mol l^{-1})	Closing error (%)
	2,4-D	2,4-DCP			
0	0.085	0.000	0.000	0.085	–
1	0.040	0.015	0.012	0.067	21.2
2	0.018	0.016	0.028	0.062	27.0
3	0.008	0.013	0.036	0.057	32.9
4	0.000	0.009	0.057	0.066	22.3

sources during the experiments. The error increased with time and reached up to 66% at four hours despite decreased concentrations of aromatic intermediates, possibly due to increased concentrations of aliphatic intermediates.

Dechlorination and mass balance

Halogen content in hazardous organics is considered as their toxicity indicator. Dechlorination efficiencies in 2,4-D degradation were higher (varied between 65% and 87%) than TOC removal in this investigation. Mass spectra of aromatic intermediates in the preliminary LCMS/MS analysis also indicated absence of chlorine atoms except in 2,4-DCP, which can be taken as evidence of efficient dechlorination. Dechlorination increased from acidic to neutral pH conditions (87%), and then decreased towards the alkaline region. But it increased with flow rate and solution temperature although the differences were not big. Dechlorination efficiencies at one hour intervals in carbon mass balance experiments (Table 1) are illustrated in Table 3. The efficiency increased with time and reached 85% in four hours.

Chloride mass balance in 2,4-D solution at one-hour intervals with no pH adjustment and solution temperature fixed at 20 °C is depicted in Table 4. The closing errors varied between 21% and 33%, which were big indeed. The big discrepancies in chloride mass balance can be mainly attributed to formation of hypochlorous, chlorous, chloric and perchloric acids by successive oxidation of chloride ions with OH radical resulting in lower chloride ion concentrations. This explanation did indicate that actual dechlorination efficiencies were bigger than those calculated based on the measured chloride concentrations. Actual dechlorination efficiencies appeared to be more than 90% in four-hour oxidation.

Conclusions

Photocatalytic degradations of 0.045 mmol l^{-1} 2,4-D solution with the new TiO$_2$ fiber catalyst and UV irradiation were, in general, similar to those with high 2,4-D concentrations investigated elsewhere. The degradations were enhanced with bigger flow rates, fixed solution temperatures and no pH adjustment cases as evidenced by bigger degradation rate constant. 2,4-D mineralization in terms of TOC removal also was significantly higher (>60%) without pH adjustment than with its adjustment (<50%). TOC removal rate constant values in the former were about two-fold bigger than the latter. Unlike 2,4-D

degradation, TOC removals were bigger at neutral and slightly acidic conditions. CO_2 gas measurement and carbon-mass balance was carried out for the first time, where about 34% organic carbon converted into CO_2 gas during four-hour oxidation. 2,4-DCP, phenol, benzyl alcohol and two unknowns (RT $\approx$ 2.65 and 3.78 min) were aromatic intermediates detected in HPLC analysis while phenol was the new aromatic. Despite low 2,4-D mineralization with initial pH adjustments, dechlorination efficiencies were very high ($>70\%$) in all the cases, which was evidenced by mass spectra of the intermediates in LCMS/MS analysis. Chloride mass balance indicated higher dechlorinations ($>90\%$) than from direct chloride measurement. Bigger flow rates and solution temperature fixed at 20 °C without initial pH adjustment were efficient for 2,4-D mineralization. This investigation results are expected to be an important basis for the application of this treatment method for dioxin-contaminated water and wastewater.

Y. Terashima *et al.*

References

Brillas, E., Calpe, J.C. and Cabot, P. (2003). Degradation of the herbicide 2,4-dichlorophenoxyacetic acid by ozonation catalyzed with Fe^{2+} and UVA light. *Applied Catalysis B: Environmental*, **46**, 381–391.

Chu, W., Chan, K.H., Kwan, C.Y. and Lee, C.K. (2004). The system design of UV-assisted catalytic oxidation process- degradation of 2,4-D. *Chemosphere*, **57**, 171–178.

Djebbar, K. and Sehili, T. (1998). Kinetics of heterogeneous photocatalytic decomposition of 2, 4-dichlorophenoxyacetic acid over titanium dioxide and zinc oxide in aqueous solution. *Journal of Pesticide Science*, **54**, 269–276.

Drezewicz, P., Trojanowicz, M., Zona, R., Solar, S. and Gehringer, P. (2004). Decomposition of 2, 4-dichlorophenoxyacetic acid by ozonation, ionizing radiation as well as ozonation combined with ionization radiation. *Radiation Physics and Chemistry*, **69**, 281–287.

Geissen, S.-U., Xi, W., Weidemeyer, A., Vogelpohl, A., Bousselmi, L. and Ghrabi, A. (2001). Comparison of suspended and fixed photocatalytic reactor systems. *Water Science and Technology*, **44**(5), 245–249.

Ishikawa, T. (2004). Photocatalytic fiber with gradient surface structure produced from a polycarbosilane and its applications. *International Journal of Applied Ceramic Technology*, **1**(1), 49–55.

Lee, Y., Lee, C. and Yoon, J. (2003). High temperature dependence of 2,4-dichlorophenoxyacetic acid degradation by Fe^{3+}/H_2O_2 system. *Chemosphere*, **51**, 963–971.

Li, X., Liu, H., Cheng, L.F. and Tong, H.J. (2003). Photocatalytic oxidation using a new catalyst-TiO_2 microsphere-for water and wastewater treatment. *Environmental Science and Technology*, **37**(17), 3989–3994.

Modestov, A.D. and Lev, O. (1998). Photocatalytic oxidation of 2,4-dichlorophenoxyacetic acid with titania photocatalyst: comparison of supported and suspended TiO_2. *Journal of Photochemistry and Photobiology A: Chemistry*, **112**, 261–270.

Mokrini, A., Oussi, D., Chamarro, E. and Esplugas, S. (1998). Photoxidation of phenol in aqueous solution. *Internet Photochemistry and Photobiology*. http://www.photobiology.com/IUPAC98/page2.htm (accessed on 23rd September 2005).

Muller, T.S., Sun, Z., MP, G.K., Itoh, K. and Murabayashi, M. (1998). The combination of photocatalysis and ozonolysis as a new approach for cleaning 2,4-dichlorophenoxyacetic acid polluted water. *Chemosphere*, **36**(9), 2043–2055.

Peller, J., Weist, O. and Kamat, P.V. (2003). Mechanism of hydroxyl radical-induced breakdown of the herbicide 2,4-dichlorophenoxyacetic acid (2,4-D). *Chemistry- A European Journal*, **9**, 5379–5387.

Piera, E., Calpe, J.C., Brillas, E., Domenech, X. and Peral, J. (2000). 2,4-dichlorophenoxyacetic acid degradation by catalyzed ozonation: TiO_2/UVA/O_3 and Fe(II)/UVA/O_3 systems. *Applied Catalysis B: Environmental*, **27**, 169–177.

Singh, H.K. and Muneer, M. (2004). Photodegradation of a herbicide derivative, 2,4-dichlorophenoxyacetic acid in aqueous suspensions of titanium dioxide. *Research on Chemical Intermediates*, **30**(3), 317–329.