Photodegradation of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans: Direct photolysis and photocatalysis processes

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Abstract

This study employed direct photolysis to treat mixed polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) solutions. The solutions included a synthetic standard 17 2, 3, 7, 8-substituted congeners solution and a practical liquid extracted from the bag filter ash of an electric arc furnace. Additionally, this work utilized a coupled catalyst (ZnO/SnO_2) under UV irradiation for photocatalytic degradation of 1, 2, 3, 6, 7, 8-HxCDD and OCDD. The direct photolysis rate of PCDFs was faster than that of PCDDs. The degradation rate of international toxicity equivalency quantity (I-TEQ) for PCDDs and PCDFs in the synthetic standard solution was 1.369 and 1.472 h^{-1}, respectively, and that in the ash-extracted solution was 0.061 and 0.117 h^{-1}, respectively. The rate of photocatalytic degradation declined as the number of chlorine atoms increased. No 2, 3, 7, 8-substituted congeners were identified during photocatalytic degradation; additionally, the photolytic rate of the UV/coupled catalyst was higher than that of UV/single catalyst system. Experimental results suggested that the primary degradation pathway for direct photolysis and photocatalysis of PCDD/Fs was the C—Cl cleavage and C—O cleavage, respectively.
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1. Introduction

There are 75 different polychlorinated dibenzo-*p*-dioxins (PCDDs) and 135 different polychlorinated dibenzofurans (PCDFs). The PCDD/Fs persist in the environment with little or no degradation [1]. The PCDD/Fs enter the environment in ultra-trace amounts from various combustion sources. More substituted-chloro dioxins typically correspond to a lower vapor pressure, and have lower solubility and higher half-life [2]. Although the presence of PCDD/Fs is a health risk to humans, only the 2, 3, 7, 8-substituted congeners are toxicologically significant.

Dioxin emission sources in Taiwan included waste incinerators, power plants, cement kilns and electric arc furnaces. The PCDD/Fs are emitted into the environment via flue gases and incineration ash. A total of 67.25 g I-TEQ/year of PCDD/Fs was discharged in Taiwan [3]. Electric arc furnaces were estimated to release 6.9 g I-TEQ/year of dioxin annually in Taiwan. The release of PCDD/Fs from this source accounts for 10.3% of total dioxin emissions in Taiwan, and, as a percentage, is significantly higher than that in other countries, which is typically have emissions from electric arc furnaces at <5% of total emissions [3]. The PCDD/Fs concentration of stack gas in electric arc furnaces was 2.2 ng/m^3 and the TEQ concentration was 0.14 ng I-TEQ/m^3 [4]. Furthermore, Chang et al. [4] indicated that >90% PCDD/Fs exist in the particulate-phase in electric arc furnaces. Various approaches have been applied to decrease PCDD/Fs emissions; these techniques either inhibit the formation of PCDD/Fs or remove PCDD/Fs from gas streams and ash. Activated carbon injection technology effectively decreases PCDD/Fs concentrations in flue gas, but increases total PCDD/Fs emissions from municipal waste incinerations [5]. Additionally, this prac-

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tice has the disadvantage of spent carbon requiring disposal. One method is to extract PCDD/Fs from spent carbon or ash and then apply an effective method for degrading the dioxins. Several methods have been considered in the development of an efficient and economically feasible approach for destroying PCDD/Fs, including catalytic destruction [6], photolysis [7–10], photocatalysis [10–12], radiolysis [13], ozonolysis [14], and biodegradation [15,16]. Although biological processes are frequently favored for contaminated site remediation, photodegradation is an effective and rapid treatment. Generally, degradation via hydroxyl radical addition is the most important mechanism for photolysis and photocatalysis for persistent organic pollutants. Photodegradation has been considered as an efficient and economically feasible technique for eliminating PCDD/Fs [7,9–12]. Those studies investigated dechlorinated products associated the degradation of different PCDD/Fs with and without the use of photocatalysts. Because non-chlorinated dioxin has little toxicity, dechlorination reactions of PCDD/Fs reduce PCDD/F toxicity. Most of studies used the synthetic standard PCDD/Fs solution to evaluate photodegradation efficiency. Moreover, no study examined the degradation efficiency of PCDD/Fs in a UV/coupled catalyst system. Hence, this study selected PCDD/Fs in bag filter ash from an electric arc furnace as parent compounds. The efficiency of direct photolysis for an ash-extracted solution and synthetic standard PCDD/Fs solution were analyzed. The photocatalytic efficiency of UV/ZnO and UV/SnO$_2$ for 1, 2, 3, 6, 7, 8-HxCDD and OCDD has been evaluated by Wu et al. [12]. Furthermore, to improve the photocatalytic efficiency of semiconductors, Serpone et al. [17] proposed an interparticle electron transfer process that couples two semiconductors with different redox energy levels to increase charge separation for corresponding conduction and valance bands. The efficiency of the photocatalytic reactions is expected to be enhanced. Hence, a UV/ZnO/SnO$_2$ system was applied to degrade 1, 2, 3, 6, 7, 8-HxCDD and OCDD. The objectives of this work were as follows: (i) identify the effectiveness of direct photolysis for a synthetic standard PCDD/Fs solution and ash-extracted PCDD/Fs solution; (ii) assess the I-TEQ photodegradation rate of PCDDs and PCDFs in both solutions under direct photolysis; and, (iii) evaluate the enhanced photocatalytic rate of 1, 2, 3, 6, 7, 8-HxCDD and OCDD in a UV/coupled catalyst system.

2. Materials and methods

2.1. Materials

Standard non-labeled and $^{13}C_{12}$-labeled 2, 3, 7, 8-position substituted PCDDs and PCDFs were purchased from Wellington Laboratories, and utilized as obtained. A 6 g bag filter ash from an electric arc furnace was spiked with known amounts of USEPA 1613 [18] internal standard solution. The XAD-2 and ash sample was Soxhlet extracted with toluene for 24 h. The toluene extract was then concentrated to approximately 1.5 ml via rotary evaporation; this solution was used as the ash-extracted solution in this work. The synthetic standard solution was prepared by mixing non-labeled 2, 3, 7, 8-position sub-

stituted PCDD/Fs according to a trend similar to that of the PCDD/Fs concentration in ash-extracted solution. The ZnO was purchased from Fluka and SnO$_2$ was purchased from Riedel-de Haen. The diameters of ZnO and SnO$_2$ powders were 27 and 59 nm, respectively. The specific surface areas of ZnO and SnO$_2$ powders were measured at 4.6 and 4.8 m^2/g, respectively, and the band gap energies were 2.92 and 4.13 eV, respectively. The corresponding maximum photoexcited wavelengths of ZnO and SnO$_2$ were 425 and 300 nm, respectively [12].

2.2. Degradation experiments

A ZnO film was coated on a quartz plate (20 mm × 20 mm) by dipping the plate into a 5 wt.% ZnO suspension and pulling it upward manually at a constant velocity. Before the plate was dipped, the quartz surface was first treated using 1% HCl, washed with distilled water and dried at 100 °C. The film was then air dried, and heat-treated in an ambient atmosphere at 400 °C for 30 min [11]. This 400 °C-sintering process was performed five times consecutively to increase the total thickness of the film [11]. The substrate was also coated with SnO$_2$ or ZnO/SnO$_2$ (w/w of ZnO:SnO$_2$ = 1/1) films using the same procedures. In direct photolysis experiments, the synthetic standard solution and ash-extracted solution was loaded onto quartz plates, the solvent was evaporated in air and the plates were then exposed to UV light. In the photocatalytic experiments, 1 μl aliquot of the parent compounds 1, 2, 3, 6, 7, 8-HxCDD and OCDD (at a concentration in nonane of 50 μg/ml) was loaded on the catalyst-coated quartz plates. The nonane was evaporated in air and the plate was then exposed to UV light. The UV light source was a 400 W medium-pressure Hg lamp (HPA-400), with a spectrum of 300–400 nm; the light intensity of the UV light was 6.33 mW/cm^2.

2.3. Analysis of PCDD/Fs

To extract the PCDD/Fs from the quartz plates, the plates were first treated using 10 ml methanol and the extractors were spiked with 20 μl of labeled PCDD/Fs standard [18]. The treated samples were further purified chromatographically using a silica gel column (70–130 mesh, Acme) with 20 ml hexane. Extracted PCDD/Fs were then analyzed at the Super Micro Mass Research and Technology Center at Cheng-Shiu University of Technology, Taiwan, using a high-resolution gas chromatographer/high-resolution mass spectrometer (HRGC/HRMS). The HRGC (Hewlett-Packard 6890, USA) has a 60 m long DB-5MS capillary column (F&W Scientific, USA), with a film thickness of 0.25 μm and column internal diameter of 0.25 mm. The oven temperature program was as follows: 150 °C for 4 min, then gradually increased to 310 °C and finally held for 5 min at 310 °C. The carrier gas was helium at a flow rate of 1.2 ml/min. The HRMS (Micromass Autospec Ultima, UK) uses a positive electron ionization detector. The analyzer mode for selected ion recording had a resolution of 10,000 (10% valley definition). The electron energy was 35 eV, and the source temperature was 250 °C [12].

3. Results and discussion

3.1. Direct photolysis of synthetic standard solution and ash-extracted solution

Analytical methods were validated by determining recovery efficiencies. The US EPA method 1613 [18] requires samples to be reanalyzed when the recovery efficiency of the $[^{13}C_{12}]$-labeled internal standards is outside the range of 30–140%. The recovery efficiencies obtained by the 1, 2, 3, 6, 7, 8-HxCDD and OCDD analyses ranged from 75 to 140%, indicating the reliability of the analytical method. Consequently, the results of PCDD/Fs quantified with reference to the known concentration of the $[^{13}C_{12}]$-labeled internal standards should be valid.

Table 1 presents a summary of initial concentrations of the combined 17 PCDD/Fs in synthetic standard and ash-extracted solutions. The 1, 2, 3, 4, 6, 7, 8-HpCDF, OCDD and OCDF are the major contributors to the PCDD/Fs concentrations for electric arc furnaces. The percentage of PCDD/Fs increases as the chlorination level of the PCDD/Fs congeners increase; this result is similar to that obtained by Chang et al. [4]. Figs. 1 and 2 plot the direct photolysis of PCDDs and PCDFs for the synthetic standard solution, respectively. The correlation coefficients are considered a measure of goodness-of-fit for the first-order kinetics, and the r^2 values for PCDD/Fs in synthetic standard solution are typically ≥0.800 (Table 2). Reaction rates followed the first-order kinetics as were also reported by other studies for dioxin photodegradation [7,9,11,19]. The average photodegradation rate constant of PCDD/Fs in synthetic standard solution demonstrated that the rate constant increased as the chlorination level of PCDD/Fs congener increased (Table 2). The photodegradation rates for PCDD/Fs generally decrease as the degree of
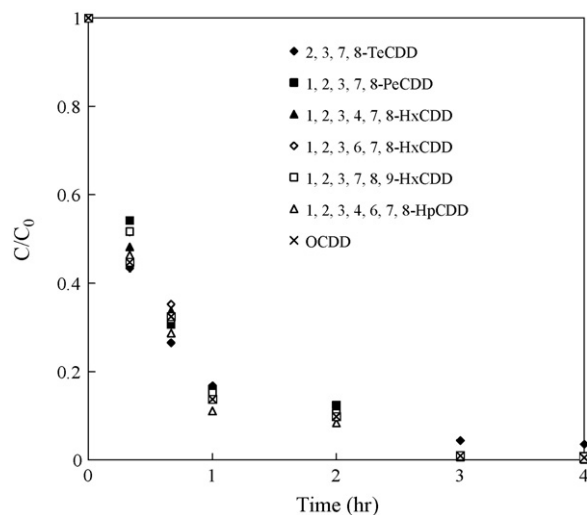

Fig. 1. Direct photolysis of PCDDs for synthetic standard solution.

chlorination increased [7,9,10]; however, this study obtained the opposite finding. Wu et al. [10] revealed that the amount of 1, 2, 3, 7, 8-PeCDD increased to maximum value and then declined during the direct photolysis of 1, 2, 3, 6, 7, 8-HxCDD; moreover, 2, 3, 7, 8-TCDD gradually increased during the reaction. Several studies have noted that dechlorination is a principal route for decomposition of PCDD/Fs by direct photolysis [6,7,9,10]. Low chlorinated PCDD/Fs can accumulate gradually during the degradation process via dechlorination from the high chlorinated PCDD/Fs [13,20]; hence, the photolysis rate of PCDD/Fs with low levels of chlorination was inhibited. As different PCDD/Fs homologues coexist in the synthetic standard solution, the photolysis rate constants of PCDD/Fs with low levels of chlorination can be influenced by the byproducts of highly chlorinated homologues. Therefore, the rate constant of direct photolysis increased as the chlorination level of the PCDD/Fs congener increased.
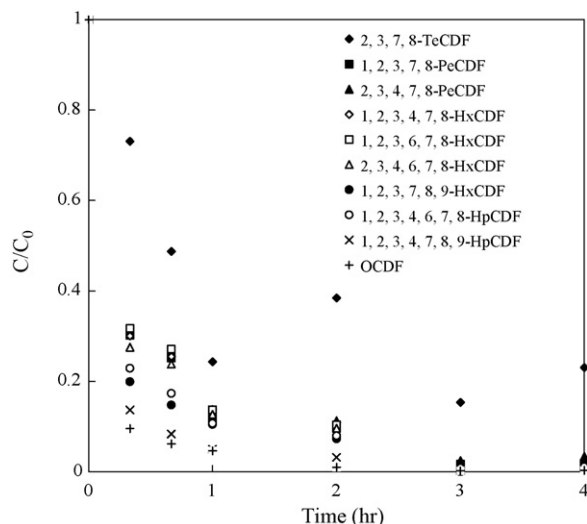
Table 1
Initial concentration of the combined 17 PCDD/Fs in synthetic standard and ash-extracted solutions

Name	I-TEFs[a]	Standard (pg)	Ash-extracted (pg)
PCDDs			
2, 3, 7, 8-TeCDD	1	1.13	0.94
1, 2, 3, 7, 8-PeCDD	0.5	14.81	3.96
1, 2, 3, 4, 7, 8-HxCDD	0.1	32.20	4.43
1, 2, 3, 6, 7, 8-HxCDD	0.1	43.37	15.05
1, 2, 3, 7, 8, 9-HxCDD	0.1	48.08	10.60
1, 2, 3, 4, 6, 7, 8-HpCDD	0.01	161.72	364.51
OCDD	0.001	600.18	2231.91
PCDFs			
2, 3, 7, 8-TeCDF	0.1	0.78	27.09
1, 2, 3, 7, 8-PeCDF	0.05	7.11	19.29
2, 3, 4, 7, 8-PeCDF	0.5	6.45	28.69
1, 2, 3, 4, 7, 8-HxCDF	0.1	14.00	25.84
1, 2, 3, 6, 7, 8-HxCDF	0.1	16.95	19.03
1, 2, 3, 7, 8, 9-HxCDF	0.1	16.04	7.68
2, 3, 4, 6, 7, 8-HxCDF	0.1	14.07	22.72
1, 2, 3, 4, 6, 7, 8-HpCDF	0.01	53.46	84.92
1, 2, 3, 4, 7, 8, 9-HpCDF	0.01	82.30	12.90
OCDF	0.001	449.04	120.74

[a] Values denoted the I-TEFs of PCDD/Fs from McKay [2].

Fig. 2. Direct photolysis of PCDFs for synthetic standard solution.

Table 2
The k-values and correlation coefficients of the synthetic standard solution in direct photolysis process

Name	k (h^{-1})	r^2	Average k (h^{-1})
PCDDs			
2, 3, 7, 8-TeCDD	1.161	0.830	1.161
1, 2, 3, 7, 8-PeCDD	1.441	0.927	1.441
1, 2, 3, 4, 7, 8-HxCDD	1.538	0.926	1.471
1, 2, 3, 6, 7, 8-HxCDD	1.515	0.932	
1, 2, 3, 7, 8, 9-HxCDD	1.361	0.944	
1, 2, 3, 4, 6, 7, 8-HpCDD	1.358	0.944	1.358
OCDD	1.487	0.937	1.487
PCDFs			
2, 3, 7, 8-TeCDF	0.598	0.913	0.598
1, 2, 3, 7, 8-PeCDF	1.398	0.841	1.316
2, 3, 4, 7, 8-PeCDF	1.234	0.877	
1, 2, 3, 4, 7, 8-HxCDF	1.496	0.877	1.547
1, 2, 3, 6, 7, 8-HxCDF	1.523	0.895	
1, 2, 3, 7, 8, 9-HxCDF	1.675	0.361	
2, 3, 4, 6, 7, 8-HxCDF	1.494	0.862	
1, 2, 3, 4, 6, 7, 8-HpCDF	1.591	0.817	1.820
1, 2, 3, 4, 7, 8, 9-HpCDF	2.049	0.765	
OCDF	2.284	0.756	2.284

Since the primary compounds in the synthetic standard and ash-extracted solutions were HxCDD/Fs, HpCDD/Fs and OCDD/Fs; this study focused on these congeners to compare the photodegradation rates for PCDDs and PCDFs. The photolysis rate constants for PCDFs homologues were higher than those for PCDDs homologues with the same chlorinated substitutions, implying that PCDDs are more resistant to photodegradation than PCDFs (Table 2). Several studies demonstrated that the photodegradation rate of PCDFs is higher than that of PCDDs [9,19,20]. One possible reason is that the total concentrations of PCDFs were lower than those of PCDDs (Table 1); therefore, the photodegradation rate of PCDFs is higher than that of PCDDs. This may also correspond with the symmetrical structure of PCDDs, which was more stable than the asymmetrical structure of PCDFs [20]. Additionally, based on the heats of formation, Koester and Hites [21] indicated that PCDDs are more stable than PCDFs due to the more negative heats of formation.

The liquid containing PCDD/Fs was prepared via extraction from real bag filter ash from an electric arc furnace using toluene. Figs. 3 and 4 present direct photolytic results. Experimental results clearly demonstrated that the ash-extracted solution was more difficult to degrade by direct photolysis than the synthetic standard solution. The HxCDD/Fs in the ash-extracted solution accumulated during direct photolysis. Since the surface of the bag filter ash can adsorb unburned organic compounds; therefore, the ash-extracted solution contained additional organics that can retard the rate of direct photolysis. Finally, the rate of direct photolysis of the ash-extracted solution was significantly lower than that of the synthetic standard solution. To identify the toxicity variation during direct photolysis, the international toxicity equivalency quantity (I-TEQ) was calculated based on appropriate international toxic equivalent factors (I-TEFs). The initial I-TEQ concentration of PCDDs and PCDFs in synthetic standard solution was 23.2 and 11.6 pg I-TEQ, respec-
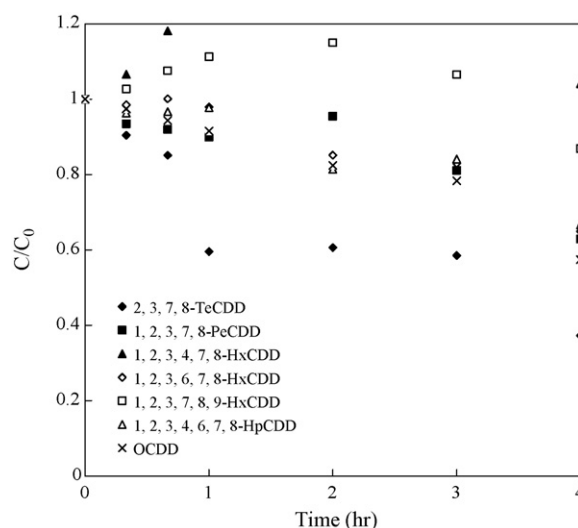

Fig. 3. Direct photolysis of PCDDs for ash-extracted solution.

tively, and that in ash-extracted solution was 11.8 and 26.6 pg I-TEQ, respectively. Due to the UV irradiation, the decrease of I-TEQ over irradiation time was obvious for both the synthetic standard solution and ash-extracted solution (Fig. 5). Particularly, detoxification was more effective for a synthetic standard solution than for the ash-extracted solution under direct photolysis (Fig. 5(b)). The degradation rate of I-TEQ for PCDDs and PCDFs in the synthetic standard solution was 1.369 and 1.472 h^{-1}, respectively, and that in the ash-extracted solution was 0.061 and 0.117 h^{-1}, respectively (Fig. 5(c)). These experimental results implied that the toxicity of the synthetic standard solution was more easily detoxified than the ash-extracted solution by direct photolysis. Regardless of whether I-TEQ is high or low, the rate of direct photolysis of the synthetic standard solution was faster than that of the ash-extracted solution; additionally, the rate of PCDFs was higher than that of PCDFs in both synthetic standard and ash-extracted solutions. This study concludes that the synthetic standard solution was more easily
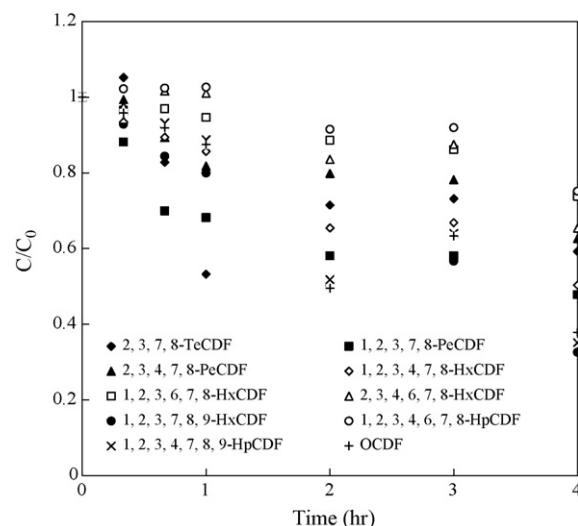

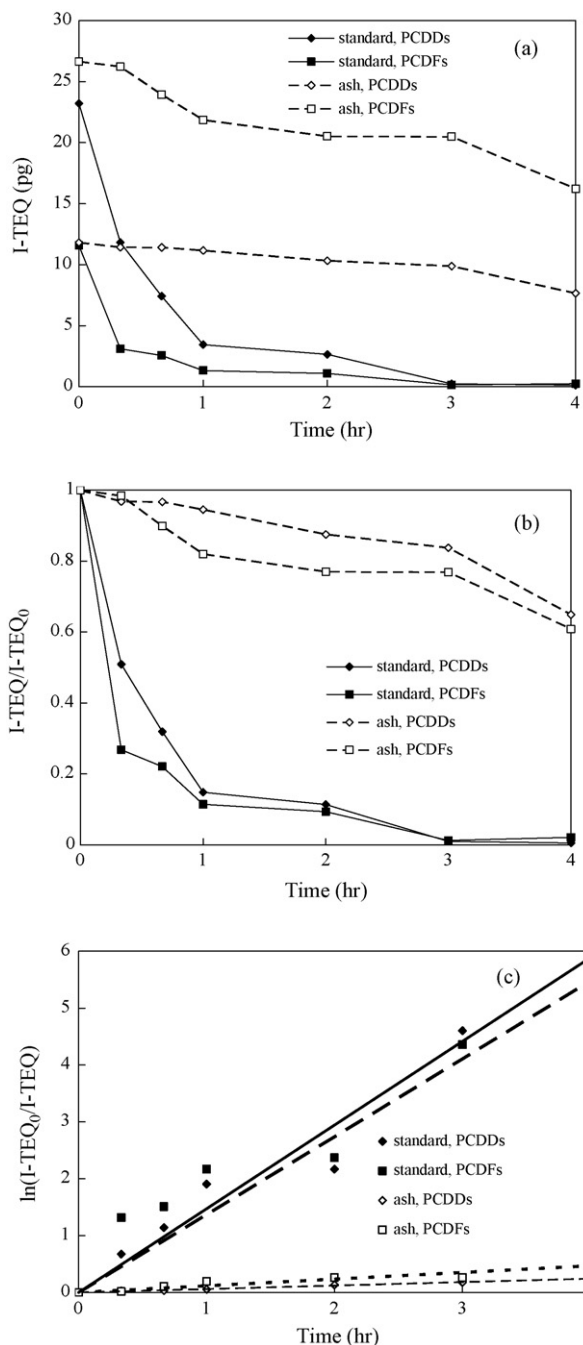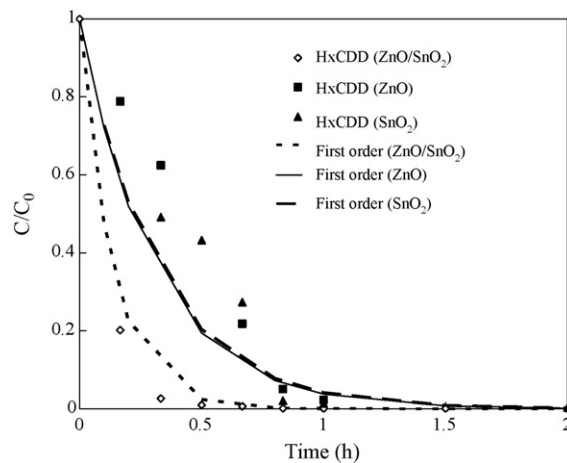Fig. 4. Direct photolysis of PCDFs for ash-extracted solution.

Fig. 6. Photocatalysis of 1, 2, 3, 6, 7, 8-HxCDD by single and coupled photocatalyst. The lines represent pseudo-first-order predicted values.
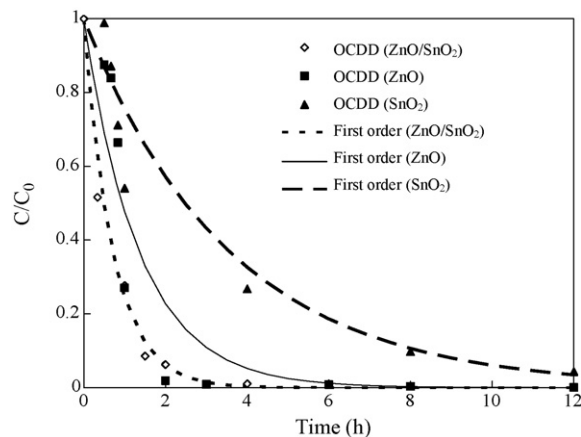

Fig. 7. Photocatalysis of OCDD by single and coupled photocatalyst. The lines represent pseudo-first-order predicted values.

OCDD in UV/ZnO, UV/SnO$_2$ and UV/ZnO/SnO$_2$. The degradation rates of 1, 2, 3, 6, 7, 8-HxCDD in UV/ZnO, UV/SnO$_2$ and UV/ZnO/SnO$_2$ were 3.28, 3.19 and 7.47 h^{-1}, respectively, and those of OCDD were 0.74, 0.28 and 1.41 h^{-1}, respectively. Photocatalysis rates declined as the number of chloro-substituent increased, suggesting that higher chlorinated PCDDs are less susceptible to photodegradation than lower chlorinated PCDDs. This may be partially due to the fact that with a large num-

Table 3
The k-values and correlation coefficients of 1, 2, 3, 6, 7, 8-HxCDD and OCDD in UV/ZnO, UV/SnO$_2$ and UV/ZnO/SnO$_2$ systems (initial PCDDs = 50 ng)

	k (h^{-1})	r^2	References
1, 2, 3, 6, 7, 8-HxCDD			
UV/ZnO	3.28	0.872	[12]
UV/SnO$_2$	3.19	0.806	[12]
UV/ZnO/SnO$_2$	7.47	0.970	This study
OCDD			
UV/ZnO	0.74	0.777	[12]
UV/SnO$_2$	0.28	0.973	[12]
UV/ZnO/SnO$_2$	1.41	0.973	This study

Fig. 5. The I-TEQ variations of synthetic standard solution and ash-extracted solution under direct photolysis process (a) I-TEQ, (b) I-TEQ/I-TEQ$_0$ and (c) first-order kinetics regression.

degraded than the ash-extracted solution; moreover, the PCDDs were more resistant to degradation by direct photolysis than PCDFs.

3.2. Photocatalytic degradation of 1, 2, 3, 6, 7, 8-HxCDD and OCDD

Figs. 6 and 7 plot the photocatalytic degradation of 1, 2, 3, 6, 7, 8-HxCDD and OCDD using immobilized ZnO/SnO$_2$. Table 3 presents the reaction rate constants for 1, 2, 3, 6, 7, 8-HxCDD and

ber of chloros on PCDDs, electron density on the aromatic ring decreased, resulting in a decreased rate of electrophilic OH addition [11]. Similar findings for the difficulty in degrading more chloro-substituted dioxins have been reported [7,9,11,13].

In direct photolysis experiments, the 1, 2, 3, 6, 7, 8-HxCDD in the synthetic standard solution was 43.37 pg and the 1, 2, 3, 6, 7, 8-HxCDD in photocatalysis experiments was 50 ng. Although the concentration of 1, 2, 3, 6, 7, 8-HxCDD in photocatalysis was markedly higher than that in direct photolysis, the photocatalytic reaction rate of 1, 2, 3, 6, 7, 8-HxCDD exceeded that of direct photolysis. The degradation rate constants follow the order of $UV/ZnO/SnO_2 > UV/ZnO > UV/SnO_2$ (Table 3). Photogenerated holes are generated after catalyst particles are irradiated with UV light. However, the rapid recombination of photoproduced electrons and holes in catalysts markedly reduces the efficiency of photocatalytic reactions [17]. The difference between the conduction band of SnO_2 and that of ZnO allows SnO_2 to act as a sink for photogenerated electrons. The holes move oppositely to electrons, and the photogenetated holes can be trapped within ZnO particles, thus increasing the charge separation efficiency. The SnO_2 particles in a coupled catalyst system $(ZnO + SnO_2)$ play an important role in photogenerated electron acceptance [22]. Externally applied bias drives away accumulated electrons via the external circuit, thus enhancing selective oxidation of PCDDs on the surface of ZnO. The improvement in charge separation achieved by coupling two catalyst systems with different energy levels improves the rate of photocatalytic degradation. Several studies have demonstrated that photocatalytic activity of the coupled catalyst was higher than that of a single catalyst system [17,22–26]. Although SnO_2 exhibited low activity because the UV light energy was partial to excite SnO_2 in a single catalyst system, SnO_2 was a suitable scavenger of photogenerated electrons in coupled catalyst systems.

This study summarized the comparisons of k-values for PCDDs in direct photolysis and photocatalysis processes (Table 4) and that for PCDFs (Table 5). The photodegradation rates for PCDD/Fs generally decrease as the degree of chlorination increased in single-compound condition (Tables 4 and 5); conversely, this study obtained the opposite finding for mixed-compound conditions (Table 2). Most works in this area focused on photolysis of PCDD/Fs in water solution, organic solvents, on plant surfaces, and in other environments [7–9,27–29]. Kluyev et al. [6] found that zero valence iron can be utilized for the stepwise dechlorination of OCDD in water at 250 °C. Ukisu and Miyadera [30] dechlorinated 2, 7-DCDD and 1, 2, 6, 7-TCDD in a solution of NaOH in propanol in the presence of carbon-supported noble metal catalyst (Pd/C and Rh-Pt/C). The catalytic destruction method depends on particular experimental conditions, such as high temperature (250 °C), alkaline conditions (in NaOH solution) or the presence of noble metal catalyst (Pd and Pt). All of these investigations have generated lower rate constants than those obtained by photocatalytic treatment herein. Therefore, photocatalysis is the best method for degradation of PCDD/Fs. The k-values follow the order of UV/coupled catalyst > UV/single catalyst > UV photolysis > sunlight photolysis. Notably, the k-value in the UV/coupled catalyst was at least one order larger than that in UV photolysis. Experimental results

Table 4
Comparisons of k-values for PCDDs in direct photolysis and photocatalysis processes

Name	System	k (h^{-1})	References
2, 3, 7, 8-TeCDD	UV	0.09	[27]
	UV	0.11	[28]
	UV	0.11	[29]
	Sunlight	0.01	[9]
	Sunlight	0.04	[28]
1, 2, 3, 7, 8-PeCDD	Sunlight	0.01	[9]
	Sunlight	0.11	[28]
1, 2, 3, 4, 7, 8-HxCDD	UV	0.01	[27]
	UV	0.18	[28]
	UV	0.18	[29]
	Sunlight	0.01	[9]
	Sunlight	0.10	[28]
1, 2, 3, 6, 7, 8-HxCDD	UV	0.07	[10]
	Sunlight	0.01	[9]
	UV/ZnO	3.28	[12]
	UV/SnO$_2$	3.19	[12]
	UV/ZnO/SnO$_2$	7.47	This study
1, 2, 3, 7, 8, 9-HxCDD	Sunlight	<0.01	[9]
1, 2, 3, 4, 6, 7, 8-HpCDD	UV	0.16	[28]
	UV	0.16	[29]
	Sunlight	0.01	[9]
	Sunlight	0.14	[28]
	UV/TiO$_2$	0.18	[11]
OCDD	UV	0.06	[7]
	UV	0.01	[27]
	UV	0.17	[28]
	UV	0.17	[29]
	Sunlight	< 0.01	[9]
	Sunlight	0.16	[28]
	UV/TiO$_2$	0.12	[11]
	UV/ZnO	0.74	[12]
	UV/SnO$_2$	0.28	[12]
	UV/ZnO/SnO$_2$	1.41	This study

demonstrated that a simple approach in which two-photocatalyst particle systems are combined increases the degradation rate, suggesting that the UV/coupled catalyst system is effective for treating PCDD/Fs.

Care must be taken to control the generation of byproducts that may be more toxic than the parent pollutants when mineralization is incomplete. The 2, 3, 7, 8-substituted PCDD/Fs products were not detected in photocatalysis experiments, perhaps due to the following reasons: (i) the photocatalytic degradation involved cleavage of the aromatic ring [11], and/or (ii) removal of lateral chloros (2, 3, 7, 8) was favored over removal of longitudinal chloros (1, 4, 6, 9) from PCDDs. Although photodegradation of OCDD in the solution phase involves preferential chloro loss at lateral positions over loss at longitudinal positions [13,31], as with HxCDD [6], congeners with longitudinal chloros degrade more rapidly than those with laterally substituted chloros in the surface-phase reaction [32]. Thus, this study speculates that photocatalysis of OCDD and 1, 2, 3, 6, 7, 8-HxCDD is that the cleavage of the aromatic ring dominating the reaction pathway. Experimental data suggested

Table 5
Comparisons of k-values for PCDFs in direct photolysis and photocatalysis processes

Name	System	k (h^{-1})	References
2, 3, 7, 8-TeCDF	UV	0.17	[28]
	UV	0.17	[29]
	Sunlight	0.02	[9]
	Sunlight	0.08	[28]
1, 2, 3, 7, 8-PeCDF	UV	0.15	[28]
	UV	0.15	[29]
	Sunlight	0.10	[28]
2, 3, 4, 7, 8-PeCDF	UV	0.10	[28]
	UV	0.10	[29]
	Sunlight	0.02	[9]
	Sunlight	0.13	[28]
1, 2, 3, 6, 7, 8-HxCDF	UV	0.23	[28]
	UV	0.23	[29]
	Sunlight	0.01	[9]
	Sunlight	0.15	[28]
1, 2, 3, 7, 8, 9-HxCDF	Sunlight	0.01	[9]
2, 3, 4, 6, 7, 8-HxCDF	Sunlight	0.01	[9]
1, 2, 3, 4, 6, 7, 8-HpCDF	UV	0.26	[28]
	UV	0.26	[29]
	Sunlight	0.01	[9]
	Sunlight	0.22	[28]
1, 2, 3, 4, 7, 8, 9-HpCDF	Sunlight	0.01	[9]
OCDF	UV	0.38	[7]
	Sunlight	<0.01	[9]

that C−Cl cleavage is a major route for PCDD/Fs in direct photolysis, and C−O cleavage may be a primary path for PCDD/Fs in the photocatalysis processes. The preferred position of hydroxyl radical attack on PCDD/Fs was dependent on the number and position of chlorine in PCDD/Fs. Seventeen 2, 3, 7, 8-substituted chlorine PCDD/Fs were detected, and 1, 2, 3, 4-TCDD, 1, 2, 3, 7-TCDD, 1, 2, 3, 8-TCDD, 1, 2, 3, 9-TCDD, 1, 3, 6, 8-TCDD, 1, 2, 8, 9-TCDD, 1, 3, 6, 8-TCDF, 1, 2, 8, 9-TCDF, 1, 2, 4, 7, 9-PeCDD, 1, 2, 3, 8, 9-PeCDD, 1, 3, 4, 6, 8-PeCDF, 1, 2, 3, 8, 9-PeCDF, 1, 2, 4, 6, 7, 9-HxCDD, 1, 2, 3, 4, 6, 7-HxCDD, 1, 2, 3, 4, 8, 9-HxCDF, 1, 2, 3, 4, 6, 8-HxCDF and 1, 2, 3, 4, 6, 7, 9-HpCDD were also detected during the experiments. Standards of all PCDD/Fs could not be obtained, so the isomers of PCDD/Fs could not be identified. Restated, only 33 chlorine PCDD/Fs (17 2, 3, 7, 8-substituted chlorine PCDD/Fs and 16 non-2, 3, 7, 8-subsituted chlorine PCDD/Fs) were identified herein. Hence, this study excludes only the byproducts from these 33 PCDD/Fs but does not describe those byproducts in detail. Since the non-2, 3, 7, 8-substitute congeners and the PCDD/Fs with low levels of chlorination were not monitored in this work; hence, the full byproduct production and reaction mechanism cannot be confirmed. Dechlorination is generally described as the predominant reaction and dechlorinated products have been identified in different solvents and under different light exposures. For a given chlorinated PCDD/Fs, when more than one degradation pathway existed, dechlorination in the most thermodynamically favored pathway occurring at the most positively charged carbon atom

in the ring, which was usually a lateral carbon atom [31]. Few studies claimed that photodechlorination is not the major pattern of PCDD/Fs degradation, proposing that C−O cleavage is an important photolytic route [7,8,11]. Rayne et al. [33] proposed that photochemical conversion from 2, 3, 7, 8-TCDD to dechlorinated PCDDs or chlorinated phenoxyphenols are minor pathways, and the chlorinated dihydroxybiphenyls may be an important route. Additionally, Rayne et al. [34] proposed that 1, 4-dibenzodioxins was rearranged to spirocyclohexadienone and biphenylquinone under UV irradiation. Experimental results demonstrated that the UV/coupled catalyst process is an effective method for degrading PCDDs; this method did not generate 2, 3, 7, 8-substituted congeners.

4. Conclusions

This study employed direct photolysis to degrade the synthetic standard solution and ash-extracted solution. The 1, 2, 3, 4, 6, 7, 8-HpCDF, OCDD and OCDF are the major contributors to PCDD/Fs concentrations in electric arc furnaces, and the percentage of PCDD/Fs increases as the chlorination level of PCDD/Fs congeners increases. Average photodegradation rate constant of PCDD/Fs in synthetic standard solution indicated that the rate constant increased as chlorination level of PCDD/Fs congeners increased. This study suggests that the PCDD/Fs with low levels of chlorination can be generated and accumulated gradually during the degradation process via dechlorination from highly chlorinated PCDD/Fs; thus, the photolysis rate of PCDD/Fs with low levels of chlorination was inhibited. The photolysis rate constants for PCDFs homologues are higher than those for PCDDs homologues with the same chlorinated substitutions, implying that PCDDs are more resistant to photodegradation than PCDFs. Experimental results demonstrated that toxicity of the synthetic standard solution was more easily detoxified by direct photolysis than the ash-extracted solution. Although SnO$_2$ showed low activity because the UV light energy was partial to excite SnO$_2$ in a single catalyst system, SnO$_2$ performed as an appropriate photogenerated-electron scavenger in coupled catalyst systems. This work suggests that C−Cl cleavage is a major route for PCDD/Fs in direct photolysis, and C−O cleavage may be a primary path for PCDD/Fs during photocatalysis.

Acknowledgements

References

[1] M.S. McLachlan, A.P. Sewart, J.R. Bacon, K.C. Jones, Persistence of PCDD/Fs in a sludge amended soil, Environ. Sci. Technol. 30 (1996) 2567–2571.

[2] G. McKay, Dioxin characterization, formation and minimization during municipal solid waste (MSW) incineration: review, Chem. Eng. J. 86 (2002) 343–368.

[3] C.M. Chen, The emission inventory of PCDD/PCDF in Taiwan, Chemosphere 54 (2004) 1413–1420.

[4] M.B. Chang, H.C. Huang, S.S. Tsai, K.H. Chi, G.P. Chang-Chien, Evaluation of the emission characteristics of PCDD/Fs from electric arc furnaces, Chemosphere 62 (2006) 1761–1773.

[5] M.B. Chang, J.J. Lin, Memory effect on the dioxin emissions from municipal waste incinerator in Taiwan, Chemosphere 45 (2001) 1151–1157.

[6] N. Kluyev, A. Cheleptchikov, E. Brodsky, V. Soyfer, V. Zhilnikov, Reductive dechlorination of polychlorinated dibenzo-*p*-dioxins by zerovalent iron in subcritical water, Chemosphere 46 (2002) 1293–1296.

[7] M. Kim, P.W. O'Keefe, Photodegradation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in aqueous solutions and in organic solvents, Chemosphere 41 (2000) 793–800.

[8] A.D. Konstantinov, A.M. Johnston, B.J. Cox, J.R. Petrulis, M.T. Orzechowski, N.J. Bunce, Photolytic method for destruction of dioxins in liquid laboratory waste and identification of the photoproducts from 2, 3, 7, 8-TCDD, Environ. Sci. Technol. 34 (2000) 143–148.

[9] J. Niu, J. Chen, B. Henkelmann, X. Quan, F. Yang, A. Kettrup, K.W. Schramm, Photodegradation of PCDD/Fs adsorbed on spruce (*Picea abies* (L.) Karst.) needles under sunlight irradiation, Chemosphere 50 (2003) 1217–1225.

[10] C.H. Wu, G.P. Chang-Chien, W.S. Lee, Photodegradation of tetra- and hexa-chlorodibenzo-*p*-dioxins, J. Hazard. Mater. 120 (2005) 257–263.

[11] W. Choi, S.J. Hong, Y.S. Chang, Y. Cho, Photocatalytic degradation of polychlorinated dibenzo-*p*-dioxins on TiO₂ film under UV or solar light irradiation, Environ. Sci. Technol. 34 (2000) 4810–4815.

[12] C.H. Wu, G.P. Chang-Chien, W.S. Lee, Photodegradation of polychlorinated dibenzo-*p*-dioxins: comparison of photocatalysts, J. Hazard. Mater. 114 (2004) 191–197.

[13] C. Zhao, K. Hirota, M. Taguchi, M. Takigami, T. Kojima, Radiolytic degradation of octachlorodibenzo-*p*-dioxin and octachlorodibenzofuran in organic solvents and treatment of dioxin-containing liquid wastes, Radiat. Phys. Chem. 76 (2007) 37–45.

[14] A. Wenzel, A. Gahr, R. Niessner, TOC-removal and degradation of pollutants in leachate using a thin-film photoreactor, Water Res. 33 (1999) 937–946.

[15] M. Bunge, H. Ballerstedt, U. Lechner, Regiospecific dechlorination of spiked tetra- and trichlorodibenzo-*p*-dioxins by anaerobic bacteria from PCDD/F-contaminated Spittelwasser sediments, Chemosphere 43 (2001) 675–681.

[16] H. Habe, K. Ide, M. Yotsumoto, H. Tsuji, T. Yoshida, H. Nojiri, T. Omori, Degradation characteristics of a dibenzofuran-degrader *Terrabacter* sp. strain DBF 63 toward chlorinated dioxins in soil, Chemosphere 48 (2002) 201–207.

[17] N. Serpone, P. Maruthamuthu, P. Pichat, E. Pelizzetti, H. Hidaka, Exploiting the interparticle electron transfer process in the photocatalysed oxidation of phenol, 2-chlorophenol and pentachlorophenol: chemical evidence for electron and hole transfer between coupled semiconductors, J. Photochem. Photobiol. A Chem. 85 (1995) 247–255.

[18] U.S. Environmental Protection Agency, Method-1613: Tetra- through Octa Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, Revision B, 1995.

[19] J. Niu, J. Chen, D. Martens, B. Henkelmann, X. Quan, F. Yang, H.K. Seidlitz, K.W. Schramm, The role of UV-B on the degradation of PCDD/Fs and PAHs sorbed on surfaces of spruce (*Picea abies* (L.) Karst.) needles, Sci. Total Environ. 322 (2004) 231–241.

[20] Z. Yang, C. Xia, Q. Zhang, J. Chen, X. Liang, Catalytic detoxification of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans in fly ash, Waste Manage. 27 (2007) 588–592.

[21] C.J. Koester, R.A. Hites, Calculated physical properties of polychlorinated dibeno-*p*-dioxins and dibenzofurans, Chemosphere 17 (1988) 2355–2362.

[22] C.H. Wu, Comparison of azo dye decolorization efficiency using UV/single semiconductor and UV/coupled semiconductor systems, Chemosphere 57 (2004) 601–608.

[23] L. Shi, C. Li, H. Gu, D. Fang, Morphology and properties of ultrafine SnO₂–TiO₂ coupled semiconductor particles, Mater. Chem. Phys. 62 (2000) 62–67.

[24] C. Wang, J. Zhao, X. Wang, B. Mai, G. Sheng, P. Peng, J. Fu, Preparation, characterization and photocatalytic activity of nano-sized ZnO/SnO₂ coupled photocatalysts, Appl. Catal. B Environ. 39 (2002) 269–279.

[25] S.C. Lo, C.F. Lin, C.H. Wu, P.H. Hsieh, Capability of coupled CdSe/TiO₂ for photocatalytic degradation of 4-chlorophenol, J. Hazard. Mater. 114 (2004) 183–190.

[26] X.H. Ou, S.L. Lo, C.H. Wu, Exploring the interparticle electron transfer process in the photocatalytic oxidation of 4-chlorophenol, J. Hazard. Mater. 137 (2006) 1362–1370.

[27] Q. Yan, S. Kapila, L.D. Sivils, A.A. Elseewi, Effects of sensitizers and inhibitors on phototransformation of polychlorinated dibenzo-*p*-dioxins (PCDDs), Chemosphere 31 (1995) 3627–3634.

[28] F. Schuler, P. Schmid, C. Schlatter, Photodegradation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in cuticular waxes of laurel cherry (*Prunus laurocerasus*), Chemosphere 36 (1998) 21–34.

[29] J. Chen, X. Quan, F. Yang, W.J.G.M. Peijnenburg, Quantitative structure-property relationships on photodegradation of PCDD/Fs in cuticular waxes of laurel cherry (*Prunus laurocerasus*), Sci. Total Environ. 269 (2001) 163–170.

[30] Y. Ukisu, T. Miyadera, Dechlorination of polychlorinated dibenzo-*p*-dioxins catalyzed by noble metal catalysts under mild conditions, Chemosphere 46 (2002) 507–510.

[31] M.M. Lynam, M. Kuty, J. Damborsky, J. Koca, P. Adriaens, Molecular orbital calculations to describe microbial reductive dechlorination of polychlorinated dioxins, Environ. Toxicol. Chem. 17 (1998) 988–997.

[32] M.H. Schoonenboom, H.E. Zoetemeijer, K. Olie, Dechlorination of octachlordibenzo-*p*-dioxin and octachlorodibenzofuran on alumina support, Appl. Catal. B Environ. 6 (1995) 11–20.

[33] S. Rayne, P. Wan, M.G. Ikonomou, A.D. Konstantinov, Photochemical mass balance of 2, 3, 7, 8-TeCDD in aqueous solution under UV light shows formation of chlorinated dihydroxybiphenyls, phenoxyphenols, and dechlorination products, Environ. Sci. Technol. 36 (2002) 1995–2002.

[34] S. Rayne, R. Sasaki, P. Wan, Photochemical rearrangement of dibenzo[1,4]dioxins proceeds through reactive spirocyclohexadienone and biphenylquinone intermediates, Photochem. Photobiol. Sci. 4 (2005) 876–886.