

Optimization of photocatalytic oxidation of 2,2',3,3'-tetrachlorobiphenyl

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Received 2 December 2003; received in revised form 9 March 2004; accepted 12 March 2004

Available online 24 April 2004

Abstract

Polychlorinated biphenyls (PCBs) are wide spread environmental pollutants. This research focused the optimum physico-chemical conditions under which photocatalytic oxidation (PCO) can be used to degrade 2,2',3,3'-tetrachlorobiphenyl (tetra-CB). Among the optimal physico-chemical conditions studied were UV intensity, hydrogen peroxide (H₂O₂) and titanium dioxide (TiO₂) concentrations, initial pH, and possible reaction intermediates were also determined. The results indicate that the optimal physico-chemical conditions necessary for the degradation of tetra-CB by PCO were UV intensity at 3.16 mW/cm², 30 mM of H₂O₂ and 100 mg/l of TiO₂. In contrast to the results of PCO studies on other organic compounds, the optimum pH for PCO degradation of tetra-CB was 5.5. The removal efficiency was also higher under acidic conditions than alkaline conditions. Although degradation intermediates such as 1,3-bis(1,1-dimethylethyl)benzene, 2,4-bis(1,1-dimethylethyl)phenol, and 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde were identified at an early stage in the reaction process, they were not completely degraded even after 7 h of PCO reaction.

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Keywords: Photocatalytic oxidation; Polychlorinated biphenyl; Optimal conditions

1. Introduction

Polychlorinated biphenyls (PCBs) are ubiquitous environmental pollutants. They are produced through the chlorination of biphenyl with anhydrous chlorine and iron filings as a catalyst. The resulting chlorobiphenyls form a complex mixture having different number of chlorine atoms per molecule [1]. Due to their chemical inertness as well as thermal and electrical insulating property, PCBs are widely used as industrial fluids (in hydraulic systems and gas turbines), dielectric fluids (capacitors and transformers), plasticizer (adhesives, textiles, sealants and copy paper), and heat exchangers [1–5]. However, PCBs are found to be neurotoxic, immunosuppressive, hepatotoxic. Accordingly, the USEPA has classified PCBs as probable human carcinogens [6–12].

Though production of PCBs was banned by the US Congress in 1976 [1,13,14], they are still being detected in

various environmental samples, including soil, sediment, animal tissues, and human breast milk [15–21]. Several treatment methods— aerobic biodegradation [22–24], Fenton's reagent [25,26] and photocatalytic oxidation [27–30]—have been studied for the remediation of PCB contaminated sites. Photocatalytic oxidation (PCO) uses a semiconductor as a photocatalyst to capture light energy and produce the high oxidizing hydroxyl radical (OH•) to degrade various compounds. The advantage of PCO over other treatment methods is its high efficiency and non-selectivity. In addition, the photocatalyst is non-toxic and inexpensive because it can be separated from the treatment stream and reused. Further, the process does not add additional chemicals to the effluent stream [30].

Although there have been studies on the use of PCO in degrading PCBs, they have tended to focus on mono- or di-chlorobiphenyls [27–30]. As yet, no study has reported on the use of PCO to degrade highly chlorinated PCBs. This research examined the degradation of a highly chlorinated PCB congener, 2,2',3,3'-tetrachlorobiphenyl (tetra-CB) by

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PCO treatment. In addition, the optimal physico-chemical conditions, including UV intensity, concentrations of hydrogen peroxide and titanium dioxide concentrations, and pH of the reaction solution were also determined. Lastly, the tetra-CB PCO degradation intermediates/product(s) were determined using gas chromatography–mass spectrometry.

2. Materials and methods

2.1. Chemicals

The 2,2',3,3'-tetrachlorobiphenyl (tetra-CB) was purchased from the Ultra Scientific Chemical Company Ltd. (North Kingstown, RI). Stock solutions were prepared by dissolving the PCB into 50 ml of HPLC-grade methanol (Mallinckrodt, Paris, KY) and kept in darkness at 4 °C prior to use. The titanium dioxide (TiO₂, Degussa P25) was a gift from the Degussa Corporation (Frankfurt, Germany). The hydrogen peroxide (H₂O₂, 35 wt.%) was purchased from Riedel-de Haën (Seeize, Germany), and the hexane purchased from Mallinckrodt (ChromAR[®] HPLC grade, 95% *n*-hexane, Paris, KY). Milli-Q water, which was purified by a Milli-Q Academic Water System and a reverse osmosis system (Ultrapure Ionex Cartridge with Millipak, Millipore, Bedford, MA) was used in all experiments.

2.2. Optimization of photocatalytic oxidation

The reaction was carried out in a reactor with a Pyrex column placed in the center (50 cm × 2 cm internal diameter, 1 mm thick, and 160 ml in volume). The reaction volume was 100 ml with desired concentrations of TiO₂, H₂O₂ and tetra-CB. The initial pH was adjusted when the experiment called for studying the effect of pH on degradation.

The Pyrex column was surrounded by eight ultraviolet (UV) lamps (15 W, 0.5 mW/cm² each, Vilber-Lourmat,

model T-15L/8D, Vernon Hills, USA) that were connected to a control panel to turn on or off the UV light. The principal wavelength of the light emitted by these lamps was 365 nm. A stainless steel cylinder covered the whole reactor to prevent the escape of UV light. An electric blower (National Silent Design 1500 EH 5941, 1400 W, Osaka, Japan) was set on the top of the stainless steel cylinder to provide ventilation and cooling for both the reaction column and the matrix during the reaction.

2.3. Determination of tetra-CB concentration

A gas chromatograph coupled with a micro-electron capture detector (GC-μECD, Hewlett Packard (HP) 6890N GC system, Wilmington, USA) was used to measure the concentration of tetra-CB in solution. Ten milliliter of tetra-CB solution was sampled at different time intervals (0, 15, 30, 45 and 60 min) and shaken with 2 ml of hexane for 1 h at 360 rpm. One milliliter of the organic portion was then sampled and the residual water content removed by passing it through a syringe with a 0.45 μm PTFE membrane (Gelman Laboratory, Ann Arbor, MT) covered with sodium sulfate (BDH Laboratory Supplies, Poole, England). The dehydrated sample was transferred to a 1.5 ml vial with an airtight screw cap (Agilent, Woodinville, England). Extracts were stored at 4 °C before analysis. The analytical conditions of GC-μECD are shown in Table 1.

The concentration of tetra-CB was detected using the GC–MS method mentioned in Section 2.5 with PCO efficiency expressed as removal efficiency (RE in %) calculated by the following equation:

$$RE = \frac{A_1 - A_2}{A_1} \times 100\% \quad (1)$$

where A_1 and A_2 are the peak areas of tetra-CB before and after PCO treatment.

Table 1

Analytical conditions for quantitative analysis of tetra-CB by GC-μECD and determination of PCO degradation intermediates/product(s) by GC–MS

	GC-μECD	GC–MS
Carrier gas-velocity	Helium (He) 1.4 ml/min	Helium (He) 1.4 ml/min
Makeup gas-velocity (for GC-μECD)	Nitrogen (N ₂) 60 ml/min	Not applicable
Column	HP-5 MS column of 5% phenyl methyl silicone	HP-5 MS column of 5% phenyl methyl silicone
Oven temperature program	Initial temperature 80 °C, hold 2 min; change to 200 °C at 30 °C/min; rise to 320 °C at 10 °C/min, hold for 5 min	Initial temperature 50 °C, hold 2 min; change to 160 °C at 10 °C/min; increase to 190 °C at 1 °C/min; rise to 270 °C at 2 °C/min
Injector port temperature	280 °C	280 °C
Detector port temperature (for GC-μECD)	330 °C	Not applicable
Transfer port temperature (for GC–MS)	Not applicable	280 °C

2.4. Statistical analysis

All experiments were performed in triplicate and one-way ANOVA used to analyze the REs between different reaction times (SigmaStat version 2.0, SPSS Inc., Chicago, IL).

2.5. Identification of PCO intermediates/products

Gas chromatography–mass spectrometry (GC–MS) was used to identify the PCO degradation intermediates/products. Five 10 ml samples were collected at various reaction times (0, 120, 180, 240, 300, 360, 480, 960 and 1440 min) for analysis. Each sample was extracted by shaking at 360 rpm at 25 °C with 2 ml *n*-hexane for 60 min. The organic portions of the five extracts were combined and concentrated to 0.5 ml using a nitrogen evaporator (Associates Inc., Organomation N-Evap, Berlin, MA), and then transferred into a 1.5 ml vial with a screw cap and stored at 4 °C before GC–MS analysis. Degradation intermediates/products were determined by GC–MS using a Hewlett Packard (HP) 6890N GC coupled with a HP 5973 mass selective detector and a HP 7683 auto-injector. One microliter of sample was injected in split-less mode for analysis. The analytical conditions are shown in Table 1.

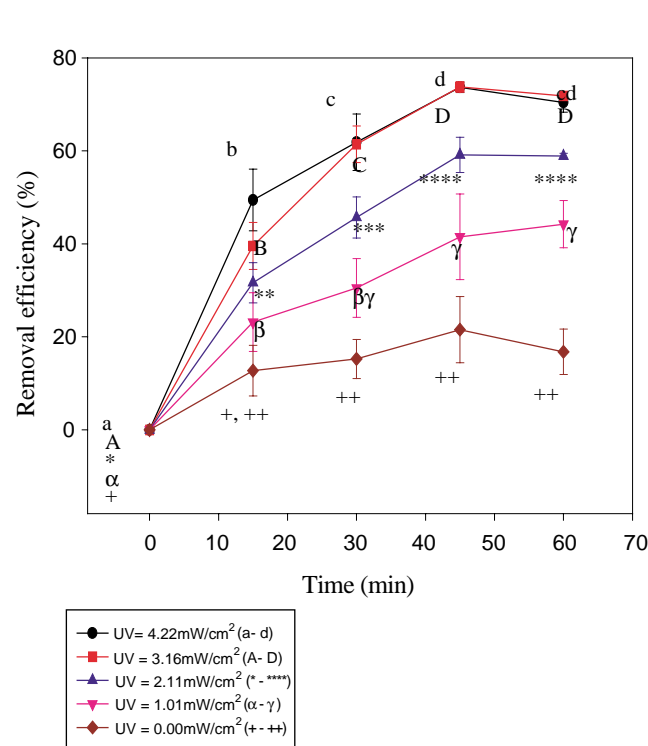


Fig. 1. Effect of UV intensity on tetra-CB removal efficiency (RE, %) of PCO reaction. Experimental conditions: Tetra-CB concentration, 15.6 $\mu\text{g/l}$; H_2O_2 concentration, 30 mM; TiO_2 concentration, 100 mg/l; pH, 5.5 and reaction volume, 100 ml of Milli-Q[®] water. Data error bars represent the mean and standard deviations, respectively, of triplicates. Means with the same letter or number of symbol are statistically identical (one-way ANOVA followed by Tukey test, $P < 0.05$). Letters and symbols representing the different data line as indicated in figure legend.

3. Results and discussion

3.1. Optimization of photocatalytic oxidation

3.1.1. Effect of UV intensity

The results presented in Fig. 1 indicate that as UV intensity increased, tetra-CB RE intensity increased up to 3.16 mW/cm². There was no statistically significant difference ($P < 0.05$) between RE of 3.16 mW/cm² and 4.22 of UV irradiation (Fig. 1, $P < 0.05$). The results are similar to other research where the efficiency of the PCO reaction increased linearly with UV intensity up to a point, beyond which no further increases were observed [31]. It is possible that the TiO_2 surface was fully utilized at 3.16 mW/cm² of UV and the excitation of electron–hole pair by UV irradiation was a maximum at that point. If so, further increases in UV intensity would have no additional effect on the rate of production of OH^\bullet or the RE of tetra-CB.

3.1.2. Effect of H_2O_2 concentration

H_2O_2 was added to enhance production of OH^\bullet through a series of redox reactions [32–34] under the assumption that H_2O_2 can enhance the removal of tetra-CB. As the H_2O_2

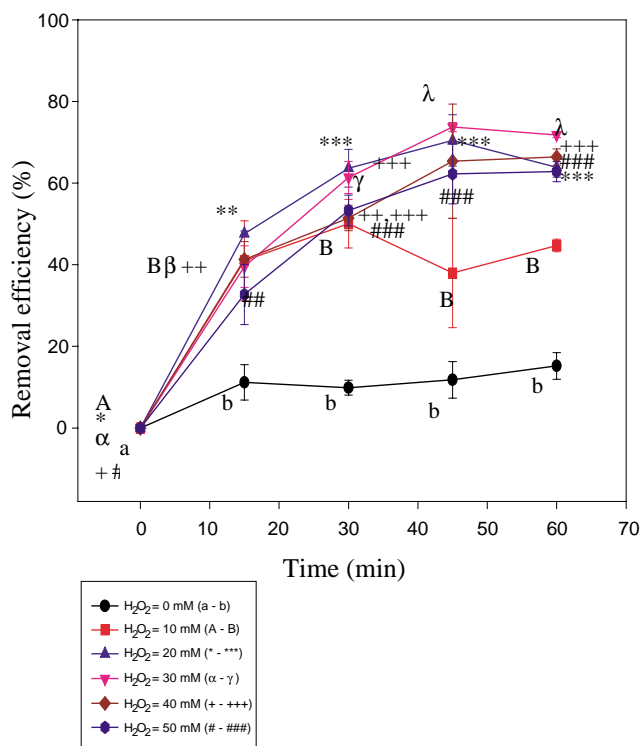


Fig. 2. Effect of H_2O_2 concentration on tetra-CB removal efficiency (RE, %) of PCO reaction. Tetra-CB concentration, 15.6 $\mu\text{g/l}$; UV intensity, 3.16 mW/cm²; TiO_2 concentration, 100 mg/l; pH, 5.5 and reaction volume, 100 ml of Milli-Q[®] water. Data error bars represent the mean and standard deviations, respectively, of triplicates. Means with the same letter or number of symbol are statistically identical (one-way ANOVA followed by Tukey test, $P < 0.05$). Letters and symbols representing the different data line as indicated in figure legend.

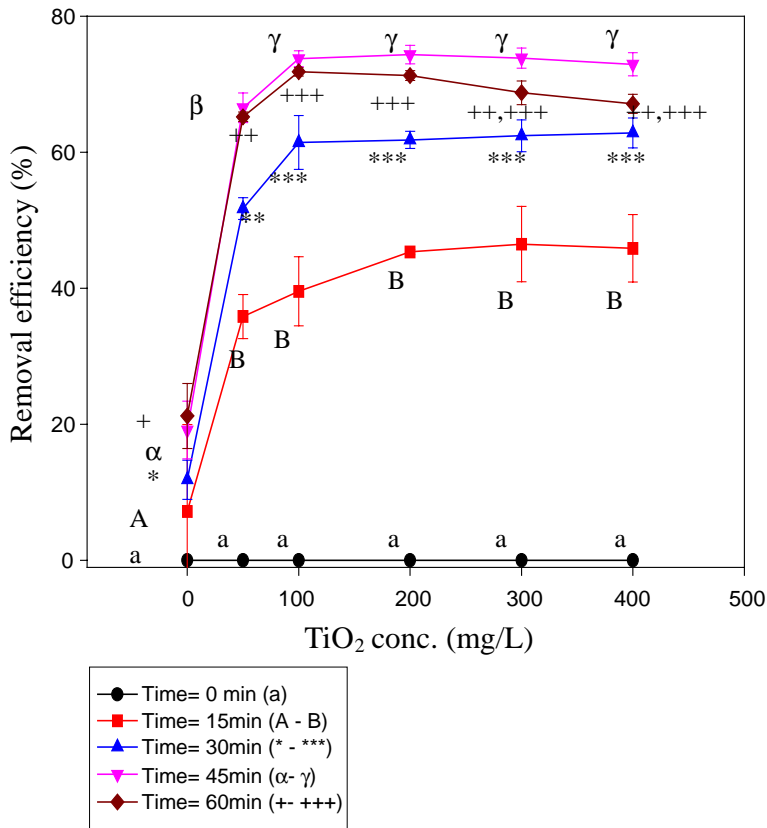


Fig. 3. Effect of TiO₂ concentration on tetra-CB removal efficiency (RE, %) of PCO reaction. Experimental conditions: Tetra-CB concentration, 15.6 μg/l; UV intensity, 3.16 mW/cm²; H₂O₂ concentration, 30 mM; TiO₂ concentration, 100 mg/l; pH, 5.5 and reaction volume, 100 ml of Milli-Q[®] water. Data error bars represent the mean and standard deviations, respectively, of triplicates. Means with the same letter or number of symbol are statistically identical (one-way ANOVA followed by Tukey test, *P* < 0.05). Letters and symbols representing the different data line as indicated in figure legend.

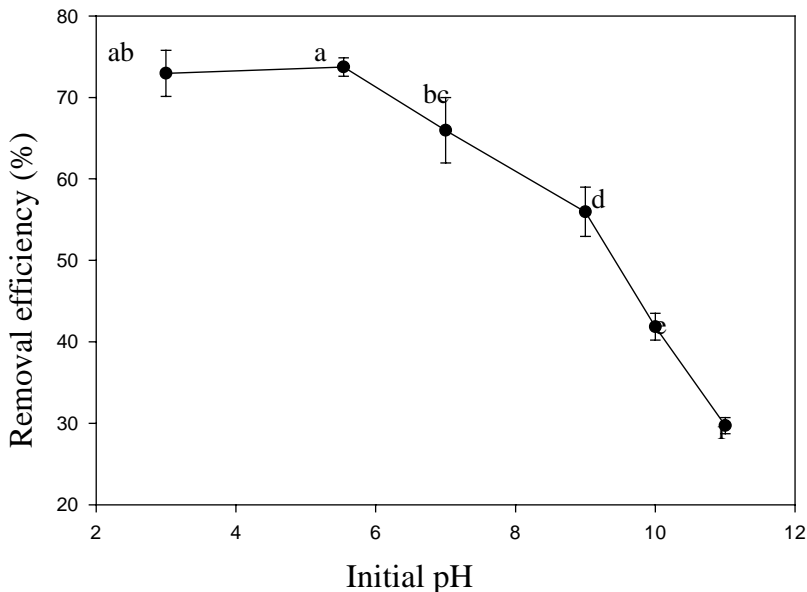


Fig. 4. Effect of pH on tetra-CB removal efficiency (RE, %) of 45 min PCO reaction. Experimental conditions: Tetra-CB concentration, 15.6 μg/l; UV intensity, 3.16 mW/cm²; H₂O₂ concentration, 30 mM; TiO₂ concentration, 100 mg/l; and reaction volume, 100 ml of Milli-Q[®] water. Data error bars represent the mean and standard deviations, respectively, of triplicates. Means with the same letter or number of symbol are statistically identical (one-way ANOVA followed by Tukey test, *P* < 0.05). Letters and symbols representing the different data line as indicated in figure legend.

concentration increased from 0 to 30 mM, the tetra-CB RE did increase (Fig. 2). However, H_2O_2 is a OH^\bullet scavenger, so the excess H_2O_2 , OH^\bullet produced was quenched by the H_2O_2 rather than reacting with the tetra-CB [35]. Moreover, as the rate of OH^\bullet generation increased, the reaction between OH^\bullet became faster; even faster than the rate of oxidation of the organic pollutants by OH^\bullet . As a result, the OH^\bullet were quenched by themselves and not available to oxidize the organic pollutants [33,35–38].

3.1.3. Effect of titanium dioxide concentration

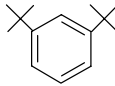
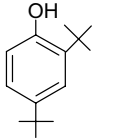
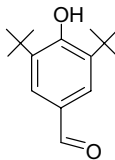
TiO_2 is a photocatalyst that absorbs UV energy and produces reactive oxygen species (ROSs) such as OH^\bullet , hydroperoxyl radical (OOH^\bullet) and superoxide ion ($\text{O}_2^{\bullet-}$) [32,38]. Increasing the concentration of TiO_2 can enhance the production of these ROSs and lead to the greater removal of target organics. The results of our research indicated that increases in the TiO_2 concentration were associated with increases in tetra-CB RE (Fig. 3). However, when the TiO_2 concentration was beyond its optimum range the RE leveled off, and even decreased slightly (Fig. 3). The reduction in overall removal efficiency is probably due to the scattering affect the high concentration of TiO_2 had on UV [39].

3.1.4. Effect of initial pH

In acidic to neutral pH solutions, the tetra-CB RE level was high. As solution pH increased, however, the tetra-CB

Table 2

The intermediates/product(s) of PCO degradation of tetra-CB detected by GC–MS

Compound	Structure
1,3-Bis(1,1-dimethylethyl)benzene	
2,4-Bis(1,1-dimethylethyl)phenol	
3,5-Di-tert-butyl-4-hydroxybenzaldehyde	

RE level decreased (Fig. 4). This is contradictory to findings in previous studies where acidic pH suppressed the formation of OH^\bullet [40,41]. Results from these other studies suggested that OH^\bullet was generated mainly from the oxidation of water by the positive hole (h^+) at lower pH levels, while the electron reduction of oxygen (dissolved oxygen, DO) was the dominant reaction at higher pH levels [29]. Since the PCO reaction was not aerated in this study, the DO level was relatively low. Thus, at high pH levels, the production of

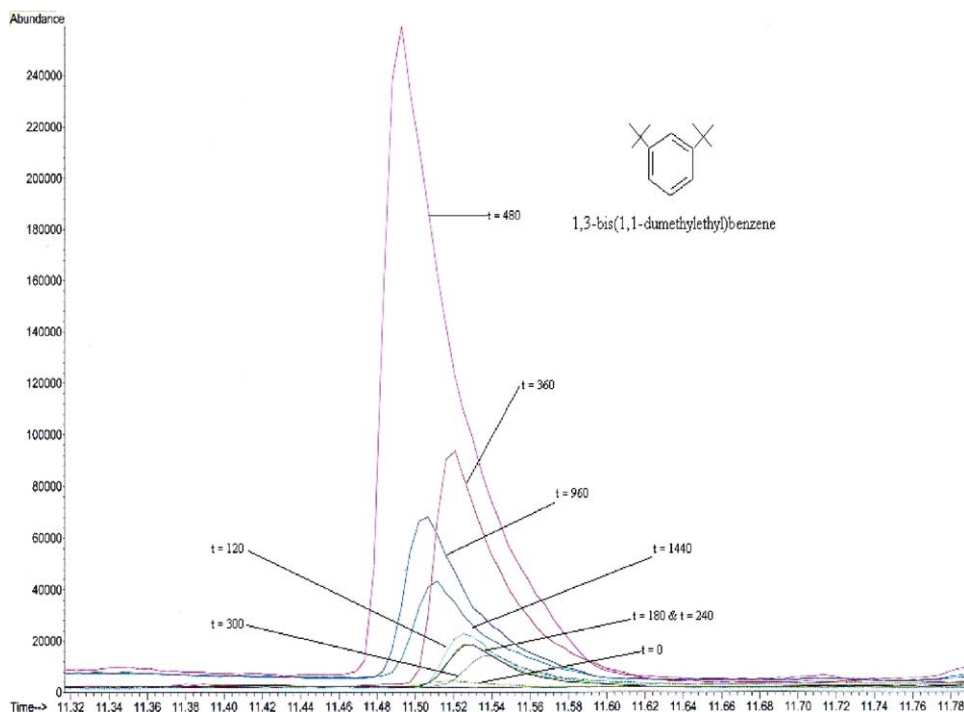


Fig. 5. Chromatogram of GC–MS after various time (in min) of PCO reaction. Structure and chemical name shown is the intermediate identified by GC–MS system. GC–MS condition as shown in Table 1.

OH• was slower and the RE level decreased. If the optimum conditions described above are used, it appears that ~80% of the tetra-CB can be removed within 60 min of reaction.

3.2. Identification of PCO intermediates

In order to accumulate more intermediates/products, a prolonged-irradiation period (120 min) was utilized for detection (no intermediates were detected after 5–15 min PCO reaction). Among the intermediates identified in Table 2, 1,3-bis-(1,1-dimethylethyl)benzene showed a time-dependent change in peak height (Fig. 5). The peak height increased with time suggesting that it was produced by the PCO reaction. After 480 min, the peak height decreased, suggesting that further degradation of 1,3-bis-(1,1-dimethylethyl)benzene was followed. The other two intermediates produced during the prolonged PCO reaction—2,4-bis(1,1-dimethylethyl)phenol and 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde—did not show time-dependent changes. Their peak heights neither increased nor decreased with treatment time.

In other studies of PCO, 2-monochlorobiphenyl, monochlorophenyl phenols, 2-chlorobenzaldehyde, 1-(2-chlorophenyl)ethanone, aldehydes, ketones, and organic acids were identified as major intermediates [29,31]. In the present study these compounds could not be detected. It is possible that the initial concentration of the parent compound used in this study was much lower than that utilized in other work and the intermediates not identifiable since their concentrations were lower than the detection limits of GC–MS. It could also be that following the reaction period, the intermediates were somehow further degraded and could not be detected.

4. Conclusions

This study investigated the PCO degradation of a highly chlorinated biphenyl congener, 2,2',3,3'-tetrachlorobiphenyl (tetra-CB). Results of the present study indicate that PCO is an effective method of degrading tetra-CB. At least 80% of tetra-CB was degraded by PCO within 60 min under optimal conditions (pH 5.5, with 30 mM of H₂O₂ and 100 mg/l of TiO₂, and irradiated by 3.16 mW/cm² UV). The presence of too much TiO₂ or H₂O₂ will reduce the tetra-CB RE, probably due to inhibition in the production of OH•, the major oxidizing species in the PCO process. The intermediates identified in this study included alkyl benzene, alkyl phenol and alkyl benzaldehyde.

A more thorough study is needed to better understand the determination of degradation intermediate(s) of highly chlorinated PCBs. In this study, the initial concentration of PCB was very low, hindering the detection of intermediates. A more effective method is needed that can concentrate the intermediates to meet the detection limits of GC–MS than that used in the present study.

Acknowledgements

This research project was supported by a grant from the Research Grant Council, Hong Kong SAR Government and a grant from the Research Committee of The Chinese University of Hong Kong to P.K. Wong.

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