

Decontamination of Industrial Waste Water by Photocatalytic Oxidation of Organic Components: A Model Study

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Industrial waste water which was highly loaded by chlorinated (50 mg AOX l⁻¹) and other organic compounds was decontaminated by laboratory-scale photooxidation of these organic impurities in the presence of oxygen and titanium dioxide as photocatalyst. The disappearance of the organic compounds was determined as a function of the irradiation time. Some contaminants such as chlorobenzene, trichloroethylene and trichloromethane were photolyzed separately in order to obtain information on the course and stoichiometry of the photooxidation.

Reinigung von Industrieabwasser durch photokatalytische Oxidation der organischen Verbindungen (Modellstudie). Industrieabwasser, das mit chlorierten (50 mg AOX l⁻¹) und anderen organischen Verbindungen hoch belastet war, wurde durch Photooxidation im Labormaßstab in Gegenwart von Sauerstoff und Titandioxid als Photokatalysator gereinigt. Die Abnahme der organischen Verbindungen wurde als Funktion der Belichtungszeit bestimmt. Einige Schadstoffe wie Chlorbenzol, Trichlorethylen und Trichlormethan wurden einzeln photolysiert, um Informationen über den Ablauf und die Stöchiometrie der Photooxidationen zu erhalten.

1 Introduction

The removal of chlorinated organic compounds from waste water is a difficult problem because these substances are not accessible to conventional decontamination procedures. The photooxidation by oxygen with semiconductor materials such as TiO₂ as photocatalyst seems to be a promising method to effectively remove organic impurities from waste water. Previous studies have shown that a variety of organic compounds including chlorinated materials can be photooxidized in water on a laboratory scale [1–8]. In some cases it was demonstrated that the photomineralization to H₂O, CO₂ and HCl was complete [1, 3, 9–12]. Presently, attempts are being made to extend this process from a laboratory to a technical scale [13–15].

Generally the photocatalytic oxidation has been studied for model solutions which contain only a single organic compound while industrial waste water which may contain a wide variety of organic pollutants has not been subjected to this photocatalysis. In the present investigation we studied the applicability of this method to the purification of industrial waste water. The efficiency was evaluated by a kinetic analysis. The consumption of the organic compounds was determined as a function of the irradiation time. Since a complete analysis of all organic compounds was not available their concentration was determined by the group parameter TOC (total organic carbon).

Larger organic molecules are certainly not photooxidized in one step. Accordingly, intermediates which could be even more toxic than the original contaminant may be generated during the photooxidation. Unfortunately, in the majority of previous studies the photooxidation was monitored only by the disappearance of the substrate. However, an additional time dependent analysis of the products would provide valuable information on the course and stoichiometry of the photolysis. According to these considerations we studied the photooxidation of the contaminants chlorobenzene,

benzene, trichloroethylene and trichloromethane in separate experiments. The consumption of the reactants as well as the formation of CO₂ was determined as function of the irradiation time.

2 Experimental Section

Materials and Reagents: The photocatalyst TiO₂ P-25 was used as supplied by Degussa. This material was mainly anatase. The BET-surface was 55 ± 15 m² g⁻¹ according to the supplier. The average particle size was 30 nm. Doubly distilled water was chosen as general solvent.

The industrial waste water was supplied by Wacker-Chemie GmbH, Burghausen. Samples were collected from the feed of the sewage treatment plant (waste water A) and from waste water which came from the production of silicones (waste water B). Waste water A contained pollutants from the production of polymers (polyvinylchloride and polyvinylacetate), chlorinated solvents and silicones. Chlorinated organic components were essential constituents of all waste water samples [16]. The concentration of some selected compounds and group parameters are given in Table 1. All samples were deep-frozen immediately after being collected to avoid loss of contaminants by evaporation and chemical reaction prior to photolysis.

Chlorobenzene (p.a.), trichloroethylene (p.a.) and benzene (p.a.) were supplied by Merck, trichloromethane (99%) was supplied by Aldrich. All substrates were used without further purification.

Photolysis: As photolysis cell Perkin-Elmer HS-6 round vessels (length 3.7 cm, diameter 2 cm) were used which could be sealed gas tight with a septum. The cell transmitted light above 320 nm. The photolysis cell contained 2 ml of sample solution, 2.0 mg TiO₂ and a small stirrer. For the photolysis of chlorobenzene, benzene, trichloroethylene and trichloromethane in separate experiments the concentrations of the aqueous solutions were 1.0 mM. Irradiation of all samples was carried out in a Photon Technology International setup equipped with a 450 W Xenon lamp (Osram). The light beam was focused on the photolysis cell by an elliptic mirror.

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The pH of the industrial waste water samples was adjusted to 8 by adding NaOH before irradiation. Due to the limited supply of oxygen in the sealed photolysis cells the concentrations of organic material were generally adjusted to the amount of available oxygen [17] in order to achieve complete photooxidation. Solutions of chlorobenzene, benzene, trichloroethylene and trichloromethane were left at their natural pH. All samples were vigorously stirred during photooxidation (Ika Combimag RCT magnetic stirrer, 1100 r.p.m.) to keep the catalyst suspended and to achieve a sufficient transfer of oxygen from the gas to the liquid phase. All photolyses were carried out three times. Blank solutions were kept in the dark for comparison. Photooxidation rates were reproducible to within $\pm 5\%$.

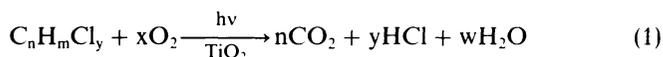
Analyses: Carbon dioxide produced during the photolyses was measured by head-space gas chromatography (Perkin-Elmer gas chromatograph 8500 equipped with a HS-6 head-space analyzer, hot-wire detector, a packed column (2 m, 1/8 in. diameter, Porapak Q, 100–120 mesh) and helium as carrier gas). The gas chromatographic measurements were calibrated by the reaction of Na_2CO_3 with HCl.

The TOC of the waste water samples was determined as CO_2 by GC after oxidation of all organic components by $\text{K}_2\text{S}_2\text{O}_8$ (90°C, 120 min). The loss of TOC during the photolysis was calculated from the amount of CO_2 generated photochemically.

Aqueous solutions of chlorobenzene, benzene, trichloroethylene and trichloromethane which were photolyzed in separate experiments were also analyzed by GC as described elsewhere [18]. The oxygen consumption during photooxidation was measured gas chromatographically (Perkin Elmer gas chromatograph as described above with packed column 2 m, 1/8 in. diameter, molecular sieve 5Å, 60–80 mesh). For calibration the initial concentration of oxygen in the aqueous solution was taken from literature data [17].

3 Results and Discussion

General: The photocatalytic oxidation of a wide variety of organic compounds in aqueous solution has been reported. The irradiation of the suspended powder of the semiconductor such as TiO_2 ($\lambda \leq 390$ nm [19]) leads to the separation of electrons and holes. Both are capable to react with species adsorbed onto the surface of the semiconductor particles. While electrons may reduce adsorbed oxygen to O_2^- the hole can oxidize adsorbed water or hydroxide ions to OH^\bullet radicals. These hydroxyl radicals are powerful oxidants which are able to oxidize many substrates at the semiconductor surface [3, 7, 8, 20–23]. It has been shown that organic compounds such as chlorocarbons are completely photomineralized according to the overall stoichiometry (1) [1, 3, 10–12, 24–26]:



The time dependent turnover can be determined by measuring the decrease of the substrates [18, 27, 28] and/or the increase of products [3, 5, 18, 24]. From these data the efficiency and the course of the photolysis can be evaluated on the basis of a suitable kinetic analysis. For the heterogeneous photocatalysis with semiconductor particles several approaches have been applied. The Langmuir-Hinshelwood kinetics [1, 3, 8, 10, 21, 25, 28–31] provides a general model which is applicable to a large concentration range. According to this model all reactive catalytic sites of the semiconductor surface are occupied when the concentration of sub-

strate is high. Therefore the efficiency of the photooxidation is limited by the number of catalytic sites available. This results in a zeroth-order kinetics. At lower concentration of substrate however, the degradation is proportional to the concentration. The reaction is now limited by diffusion to the semiconductor surface. This may result in a pseudo first-order kinetics.

These predictions were indeed confirmed experimentally. The decrease of substrate has been found to follow pseudo-first order kinetics if substrate concentration was low [11, 12, 18, 21, 23, 26, 28–30, 32, 33]. On the contrary, at high concentrations a zeroth-order kinetics was observed [18, 31, 33].

However, any simple kinetic model can not take into account special effects such as the competition of different substrates for the catalytic sites [10, 31]. In addition, an insufficient and declining oxygen supply causes complications which can be encountered in closed systems as used in our experiments.

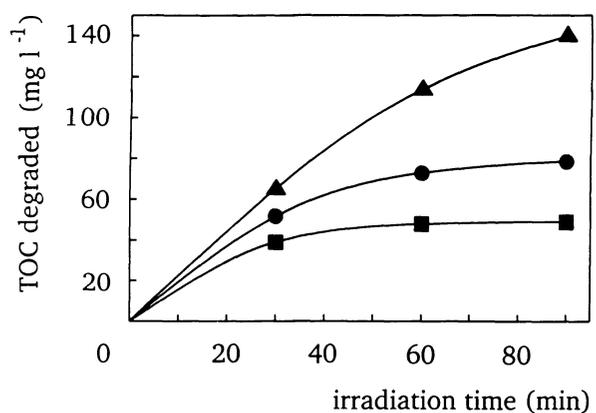


Figure 1: Photooxidation of waste water A with $563 \text{ mg TOC l}^{-1}$ (\blacktriangle), waste water A (1:10) with 52 mg TOC l^{-1} (\bullet) and waste water B (1:10) with $100 \text{ mg TOC l}^{-1}$ (\blacksquare)

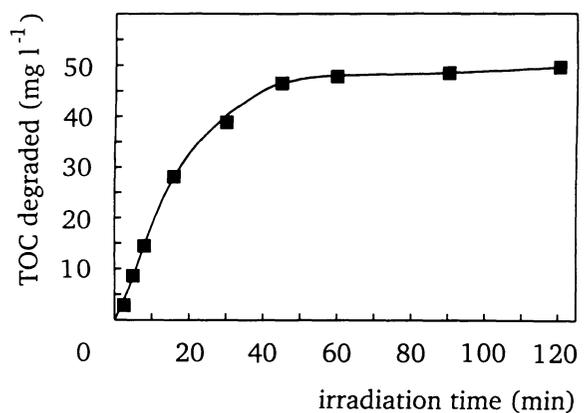


Figure 2: Photooxidation of waste water A (1:10) with 52 mg TOC l^{-1}

Industrial Waste Water: At high substrate concentrations a plot turnover versus irradiation time should result in a straight line in accord with a zeroth-order kinetics. At later stages of the photolysis a curve should be observed since the substrate concentration has reached the range of pseudo-first order kinetics. Finally, the concentration approaches a limiting value which may correspond to 100% turnover. Such a characteristic behavior was not observed for waste

water A (Fig. 1) since the amount of oxygen in the sealed photolysis cell was insufficient for a complete photooxidation [17]. However, when waste water A was diluted 1:10 the oxygen supply was sufficient and the plot showed the expected behavior (Fig. 1, 2). Similar results were obtained with diluted waste water B (Fig. 1, 3).

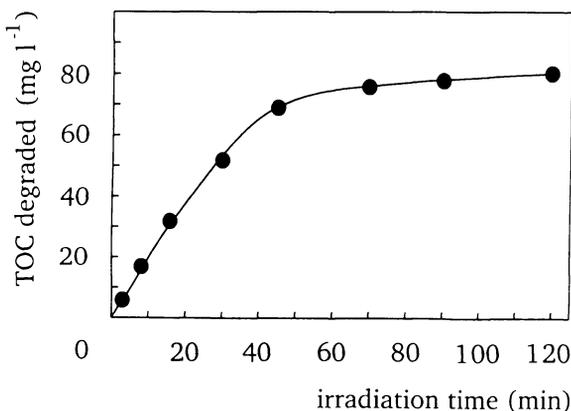


Figure 3: Photooxidation of waste water B (1:10) with 100 mg TOC l⁻¹

Table 1: Analytical characterization of waste water samples [16]

Content	Contaminant [mg l ⁻¹]	
	Waste Water A	Waste Water B
Chlorobenzene	<0.1	0.5
1,1-Dichloroethylene	<0.1	<0.1
trans 1,2-Dichloroethylene	<0.1	<0.1
cis 1,2-Dichloroethylene	<0.1	<0.1
Trichloroethylene	<0.1	<0.1
Tetrachloroethylene	<0.1	<0.1
Chloromethane	2.4	13
Chloroethane	2.5	11
Dichloromethane	4.6	2.6
Trichloromethane	0.3	<0.1
Tetrachloromethane	<0.1	<0.1
AOX	44.3	55.0
POX	6.2	22.2
TOC	563	1020
COD	1352	2539
pH	4.6	1.2

AOX: adsorbable organic halides; POX: purgeable organic halides; TOC: total organic carbon; COD: chemical oxygen demand

The inspection of Fig. 2 and 3 reveals more details. The organic constituents of diluted waste water A were almost completely photooxidized after an irradiation of 60 min (Fig. 2). After 120 min a limiting value of 92% photooxidation was reached. The residual TOC may be due to compounds such as perchlorinated alkanes (Table 1) which are photooxidized very slowly or not at all [1, 18]. Diluted waste water B showed an additional deviation (Fig. 3). Two ranges of zeroth-order behavior can be identified. The first of this region extends from 0 to about 20 min and the second from about 70 to 120 min. In the beginning an efficient photolysis took place which was almost complete after 45 min irradiation time. At later stages a less efficient photolysis occurred. Both ranges can be assigned most likely to two different compounds or groups of compounds which are photooxi-

dized with sufficiently different efficiencies. Even after an irradiation of 180 min the photooxidation of the organic constituents of diluted waste water B was not yet complete (83%).

Selected Chlorinated Organic Compounds: In the previous section it has been demonstrated that mixtures of chlorinated organic compounds can be photooxidized efficiently although it is difficult to gain a deeper insight in the course of the photolysis under these conditions. More details are revealed if single compounds instead of mixtures are photooxidized. We explored this possibility and selected typical chlorinated organic compounds for this purpose. In addition to the disappearance of the substrate the formation of CO₂ as photooxidation product was determined in order to detect the generation of intermediates and to analyze the stoichiometry of the photolyses.

For the photolysis of chlorobenzene the decrease of this substrate did not match the CO₂ production during the first 100 min of irradiation (Fig. 4). An explanation for this observation is provided in Fig. 5. In addition to the decrease of the substrate the difference between this decrease and the increase of stoichiometric amounts of CO₂ was plotted versus irradiation time. This difference gives evidence for the formation of intermediates which are generated from the beginning, reach a maximum concentration after 10 min, undergo themselves a photooxidation and are completely photooxidized at the end (120 min). It is quite understandable that larger molecules such as chlorobenzene are not photooxidized in one step.

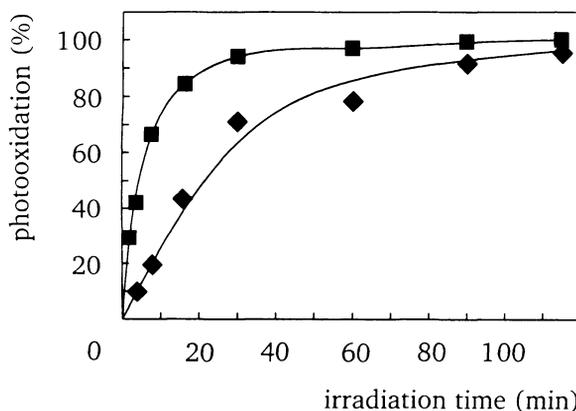


Figure 4: Photooxidation of chlorobenzene calculated by decrease in substrate (■) and increase in CO₂ (◆)

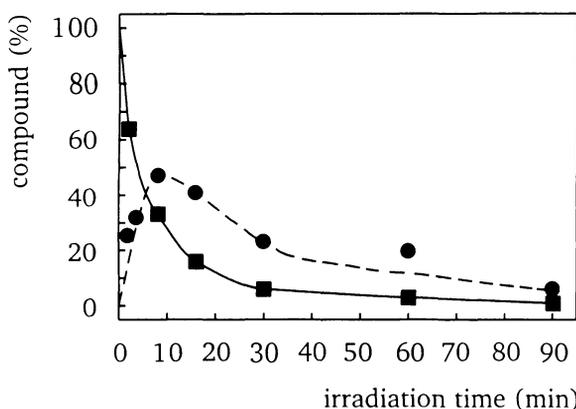


Figure 5: Photooxidation of chlorobenzene calculated by decrease in substrate (■) and intermediates during photoreaction (●)

Although benzene was not a component of the industrial waste water (see above) it was included in the present work in order to compare it with chlorobenzene. It can be concluded from Fig. 6 that in the beginning both photolyses proceed with comparable rates while at later stages the photooxidation of chlorobenzene is less efficient. It is apparently the intermediate which is responsible for this delay (Fig. 6).

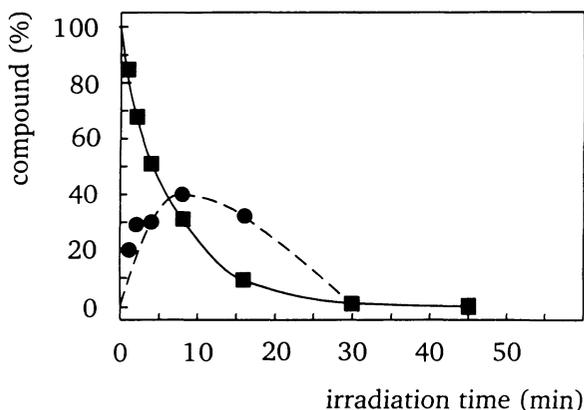


Figure 6: Photooxidation of benzene calculated by decrease in substrate (■) and intermediates during photoreaction (●)

Although we made no attempt to analyze the intermediates other investigators identified some primary photooxidation products of aromatic compounds. For example, phenol and quinone were formed as intermediates of the photooxidation of benzene [10]. Hydroxylated aromatic compounds were also detected during the photooxidation of substituted aromatics [8, 11, 21, 23, 25, 26, 31]. On the basis of our results we can conclude that in the initial attack of OH[•] radicals there is some discrimination between chlorobenzene and benzene. However, at later stages the disruption of the carbon-chlorine bonds of chlorobenzene is apparently less facile than the photooxidative breakage of carbon-hydrogen bonds.

While trichloroethylene displays a similar reactivity as chlorobenzene or benzene (Fig. 7) the photooxidation of trichloromethane occurs in one step since no intermediates were detected in the latter case. At any time of the photolysis the decrease of substrate matched the stoichiometric formation of CO₂. For trichloroethylene the aldehyde Cl₃CCHO was identified as intermediate of the photooxidation [30].

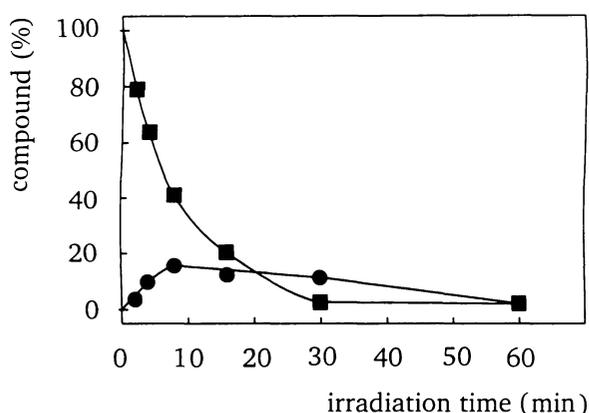


Figure 7: Photooxidation of trichloroethylene calculated by decrease of substrate (■) and intermediates during photoreaction (●)

Table 2: Experimental and theoretical equivalents for the oxygen consumption and carbon dioxide production according to equation (1) at complete photooxidation

Substrate	Oxygen equivalents		CO ₂ equivalents	
	Experimental	Theoretical	Experimental	Theoretical
Chlorobenzene	6.0 ± 1.0	7.0	5.7 ± 0.3	6.0
Trichloroethylene	1.6 ± 0.7	1.5	2.1 ± 0.2	2.0
Trichloromethane	0.5 ± 0.3	0.5	1.1 ± 0.2	1.0
Benzene	6.4 ± 1.1	7.5	6.0 ± 0.3	6.0

A complete photooxidation of chlorobenzene, benzene, trichloroethylene and trichloromethane was confirmed. At the end of the photolysis the consumption of substrate and oxygen matched the formation of CO₂ according to equation (1) (Table 2).

4 Conclusion

Although more studies are necessary to fully understand the photocatalytic oxidation of organic compounds including chlorinated hydrocarbons a technical application of this method for the decontamination of waste water seems feasible.

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