

Destruction of chlorinated pesticides in TiO₂-enhanced photochemical process

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ABSTRACT. Aqueous solutions containing 200 mg/dm³ of lindane, p,p'-DDT and methoxychlor were photodegraded for 60 min in UV/TiO₂/O₂ system. Sparged air was introduced into the reactor environment. Titanium dioxide supported on glass, hollow microspheres served as the photocatalyst. Pesticides destruction ratio was evaluated and oxidation products were identified by gas chromatography with thermionic specific detector (GC-TSD) and mass spectroscopy detector (GC-MS). The concentration of pesticides after reaction was determined in the liquid phase, in the solid phase (adsorbed on the photocatalyst) and in the gas phase. The experimental data indicates that pesticide removal with the gas phase was insignificant, therefore it was neglected in the assessment of the photodegradation efficiency. From 14% to 58% of investigated pesticides remained adsorbed on catalyst surface after photodegradation. High content of pesticides in the solid phase after reaction resulted from their low solubility in water and indicates significant adsorption ability of the pesticides by TiO₂.

1. INTRODUCTION

Lindane, p,p'-DDT and methoxychlor, formerly widely used as insecticides, entered the environment causing contamination of water and created health hazard. Various methods have been proposed for decontamination of the aquatic environment. UV-enhanced treatment of water and wastewater using titanium dioxide photocatalyst is considered to be cost effective alternative to well-established oxidation technologies such as ozonolysis or oxidation in the UV/H₂O₂ system [1]. However, separation of the dispersed catalyst requires attention and several authors suggested that supporting the catalyst should contribute to better control of the process [2]. In this regard titanium dioxide supported on glass hollow microspheres was used as catalyst.

Most investigations pertaining to photocatalytic degradation of aqueous solution of organic compounds in the presence of UV/TiO₂ involved air/oxygen sparging [1-5]. Thus, organic compounds could be removed with the gas stream (stripping) causing to secondary pollution of the atmosphere. The possibility of removal of organic compounds with the gas phase was not considered in available literature. In papers on lindane, p,p'-DDT and methoxychlor degradation, the degradation products were not determined simultaneously in the aqueous phase and on the surface of catalyst.

In this paper, mass balance of oxygen-enhanced photodegradation of lindane, p,p'-DDT and methoxychlor pertaining to three phases, *i.e.*, stripped with the gas phase, adsorbed on the catalyst surface and left in the solution after 60 min irradiation is presented. Pesticide degradation products formed in the TiO₂-UV-O₂ system are considered and determined separately in the liquid phase and on the surface of catalyst.

2. MATERIALS AND METHODS

Reagents. Easily separable titanium photocatalyst was prepared by deposition of titanium dioxide at the surface of hollow glass microspheres according to earlier developed technique [6]. The bulk density of the investigated microspheres was 0.4 g/cm³. From 0.1 to 0.5 weight percent of TiO₂ was deposited on glass microspheres, as revealed by the complexing TiO₂/H₂O₂ colorimetric method [6].

Lindane, p,p'-DDT and methoxychlor 99% purity of, were obtained from a Sigma Chemical Co. All solvents used (acetone, n-hexan, methanol) were of pesticide residue grade and were products of Merck (Darmstadt, Germany). Analytical standards of organochlorine pesticides (lindane, p,p'-DDT, methoxychlor, o,p'-DDE) were purchased from Pesticide Analytical Standard Institute of Organic Industrial Chemistry (Warsaw, Poland) with purity range 99-99.7%.

Irradiation experiments. Aqueous solutions of lindane, p,p'-DDT and methoxychlor were degraded for 60 min in the presence of sparged air. Pesticide solutions were irradiated in water-cooled laboratory UV reactor (Figure 1), equipped with Heraeus 150 W medium-pressure mercury vapor lamp. Titanium dioxide supported on glass, hollow microspheres served as the photocatalyst. 1 g of the photocatalyst was suspended in 1000 cm³ aqueous pesticide "solution", which contained 200 cm³ of the investigated pesticide. Pesticide aqueous "solution" was prepared by blending acetone pesticide solution with distilled water. Since of all three pesticides solubility in water was much below 200 mg/dm³ the feed stream used in the investigation was fine suspension. The term "solution" is further used in such understanding. Acetone was chosen as stable solvent in reaction involving hydroxyl radical [7]. The suspension

was stirred for 10 min. and then irradiated in the presence of air, which was sparged at the rate of 20 dm³/h. The gas phase from the photoreactor was directed to adsorption bulbs with cyclohexanone to trap volatile organic compounds. Some experiments were carried out without pH correction (initial pH = 6) and some were carried out using phosphate buffering solution (pH = 11).

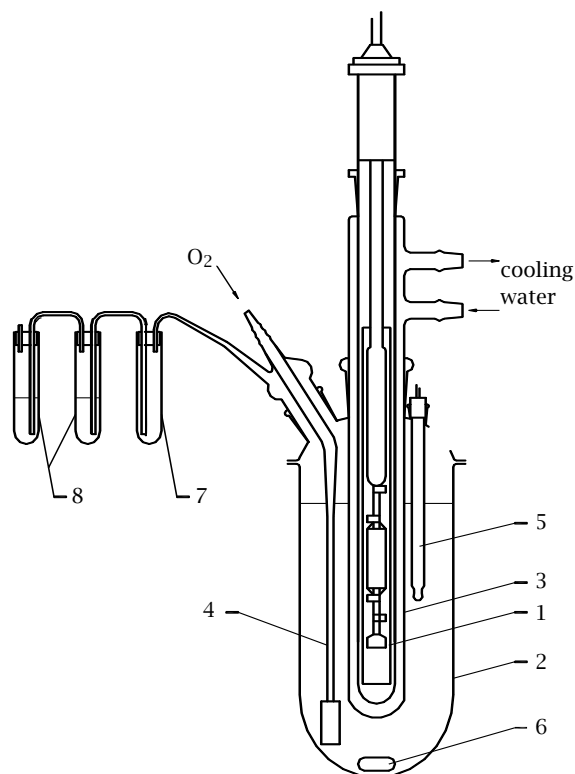


Figure 1. Schematic diagram of photoreactor for pesticide destruction: 1- Heraeus medium pressure mercury lamp, 2- glass reactor, 3- UV lamp cooling system, 4- gas sparger, 5- pH electrode, 6- stirrer, 7- drip tube, 8- absorber for volatile compounds.

Analytical procedure. Pesticides destruction ratio and identification of oxidation products were made by gas chromatography with thermionic specific detector (GC-

TSD) and mass spectroscopy detector (GC-MS). The concentration of pesticides after reaction was determined in the liquid phase, in the solid phase (adsorbed at the photocatalyst) and in the gas phase. 200 ml of filtered water sample was extracted with dichloromethane (I step: 200 : 200 v/v; II step: 200 : 100 v/v). Then, the organic layer was separated and dried over anhydrous sodium sulphate. The organic solvent was evaporated using rotary evaporator and the residue was dissolved in acetone to the final volume 10 ml. The separated catalyst was dried, extracted with 50 ml of acetone and the solvent was evaporated in rotary evaporator. The residue was dissolved in 10 ml of acetone. Cyclohexanone from the absorption bulbs was also evaporated and the residue was dissolved in 2 ml of acetone prior to injection into the gas chromatograph.

A Varian 3300 gas chromatograph with TSD system equipped with packed chromatographic column (Chromosorb WHP carrier, 100/120 mesh; liquid phase OV-225-5%; 2 m×2 mm I.D.) was used. The temperature program applied in GC-TSD was as follows:

40° C (1 min) $\xrightarrow{10^\circ\text{C}/\text{min}}$ 140° (3 min) $\xrightarrow{5^\circ\text{C}/\text{min}}$ 250° C (20 min).

All MS measurements were performed with a Hewlett Packard HP 5971 mass-selective detector combined with a HP 5890 gas chromatograph fitted with HP-5 capillary column (25 m × 0.25 mm I.D., 0.25 μm film thickness). The temperature program applied in GC-MS was as follows: 60° C $\xrightarrow{30^\circ\text{C}/\text{min}}$ 100° C $\xrightarrow{10^\circ\text{C}/\text{min}}$ 280° C (10 min). Split/splitless injection port and transfer line temperature was set to 250° C. The 5 μl sample was injected using hot splitless injection. MS measurements were performed in SCAN mode. Solvent delay was set to 4 min.

3. RESULTS AND DISCUSSION

Pesticides distribution and elimination degree during photodegradation of aqueous solution containing 200 mg/dm³ of the investigated compound is given in Table 1. After 60 min irradiation, different process efficiency was obtained. Considering possibility of pesticides removal with the gas phase, the vapor pressure of the investigated compounds is also included in Table 1.

Table 1. Pesticides distribution and elimination after 60 min irradiation (a) solution without pH correction, initial pH=6; (b) buffered solution pH=11.

Compound	Vapor pressure at 20°C [mmHg]	pH	Content of pesticide [wt. %]			Elimination [%]
			solid phase	liquid phase	gas phase	
lindane	3.26×10^{-5}	6	58.5	2.96	0.002	38.5
		11	55.8	2.9	0.04	41.2
p,p'-DDT	1.9×10^{-7}	6	39.6	0.05	0.002	60.3
		11	0	0.8	0	99.2
methoxychlor	1.43×10^{-6} *	6	19.5	0.03	0.001	80.5
		11	14.6	0.2	0.03	85.2

* at 25°C

The experimental data indicate that at the pH = 11 with increasing vapor pressure, the amount of removed pesticide increased from below 0.001% to 0.04%. At the pH = 6 pesticides concentration in gas phase was insignificant and remained within the experimental error—therefore any correlation was not found.

Considering mentioned earlier adsorption of pesticides on TiO₂ [8] the process efficiency was estimated from lindane, p,p'-DDT and methoxychlor concentration in the liquid phase and in the solid phase. From 14% to 58% of the investigated pesticides remained adsorbed on the catalyst surface after photodegradation (see Table 1). High content of pesticides in the solid phase after reaction resulted from their low solubility in water and indicates significant adsorption ability of the pesticides by TiO₂.

After 60 min irradiation lindane was eliminated only in about 40%, see Table 1 and Figure 2. About 60% of lindane was adsorbed on catalyst surface after reaction and lindane removal from the mixture with the gas phase contributed from 0.0024% to 0.04% to the overall pesticide amount. Lindane degradation products are shown in Table 2. Chlorine atom abstraction as well as addition was observed. However, ring cleavage was not detected. In the liquid phase, only α -HCH as degradation byproduct was present. Isomer α -HCH was also detected on the surface of the catalyst. Additionally 1,2,3,4,5-pentachloro-

cyclohex-1-ene, 3,4,5,6-tetrachloro-cyclohex-1-en, and 1,1,2,3,4,5,6-heptachlorocyclohexane were detected as byproducts adsorbed on microspheres. Presence of heptachlorocyclohexane, pentachlorocyclohexene and tetrachlorocyclohexene was confirmed in the literature [5]. Since only hexachlorocyclohexane was originally fed to the reactor the presence of heptachlorocyclohexane indicates the occurrence of Cl[•] radicals in the reaction environment. These radicals could originate from lindane and its degradation intermediates by homolytic scissions [5].

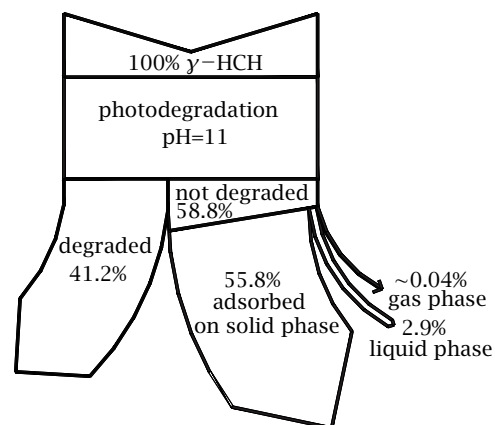


Figure 2. Sankey plot for lindane photodegradation in alkaline solution, pH=11.

Table 2. Lindane degradation products detected in the liquid and the solid phase after 60 min. irradiation.

Analyzed phase	Chemical term	CAS register number	compounds structure
liquid	α -HCH	319-84-6	
solid	α -HCH	319-84-6	
	1,2,3,4,5-pentachlorocyclohex-1-ene	28903-24-4	
	3,4,5,6-tetrachlorocyclohex-1-ene	319-81-3	
	cyclohexane, 1,1,2,3,4,5,6-heptachloro	707-55-1	

The same time of reaction resulted in 60.3% elimination of *p,p'*-DDT in unbuffered solution and in 99.2% elimination in buffered alkaline environment. *p,p'*-DDT was not detected on the solid phase and in the gas phase after irradiation in alkaline solution (see Figure 3). However, it does not indicate the mineralization of these compounds. High pH value stimulates alkaline hydrolysis of *p,p'*-DDT, therefore the elimination ratio could increase and the parent compound was not detected while transformation products were found. Bis(4-chlorophenyl) methanone was detected only in the liquid phase. Simultaneously, compounds containing from 3 to 4 Cl atoms as DDD and DDE were detected as byproducts adsorbed on the catalyst surface, see Table 3. Low water solubility of DDD and DDE ($< 1 \text{ mg/cm}^3$ and $< 0.1 \text{ mg/cm}^3$ respectively) contributed to high adsorption yield. Reaction intermediates, solvent, reaction products, other substrates can simultaneously adsorb on the surface. As for heterogeneous catalysis, this competitive adsorption will influence the observed reaction kinetics [9].

For the $\text{pH} = 6$, about 40% of *p,p'*-DDT was adsorbed on the catalyst surface after processing. Moreover, 0.002% of the pesticide was removed from the reaction environment with the gas phase. From the practical viewpoint, the results show higher efficiency of *p,p'*-DDT photodegradation carried out in alkaline solution than at lower pH. However, for both investigated pH values compounds containing only one benzene ring were

not found. Benzene ring occurred resistant to degradation at processing conditions.

Insignificant difference in methoxychlor degradation efficiency was observed for both investigated pH values. The experimental results, see Table 1, indicate that methoxychlor was eliminated from 80 to 85 percent. Methoxychlor photodegradation in alkaline solution is shown in Figure 4. About 19% of the pesticide were adsorbed on the catalyst surface after 60 min irradiation.

Methoxychlor removal with the gas phase was lower than for lindane, since the vapor pressure was smaller at the processing temperature, see Table 1.

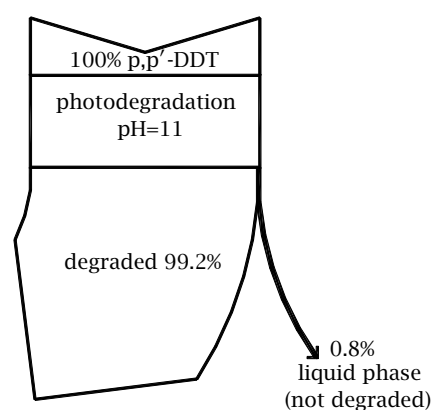


Figure 3. Sankey plot for *p,p'*-DDT photodegradation in alkaline solution, $\text{pH}=11$.

Table 3. *p,p'*-DDT degradation products detected in the liquid and the solid phase after 60 min irradiation.

Analyzed phase	Chemical term	CAS register number	compounds structure
liquid	4,4'-dichlorobenzophenone	90-98-2	
solid	1,1'-(chloro-ethenylidene) bis(4-chlorobenzene)	1022-22-6	
	methanone, (4-chlorophenyl)(2,4-dichlorophenyl)	33146-57-5	
	<i>p,p'</i> -DDE	72-55-9	
	<i>p,p'</i> -DDD	72-54-8	
	<i>o,p'</i> -DDT	789-02-6	

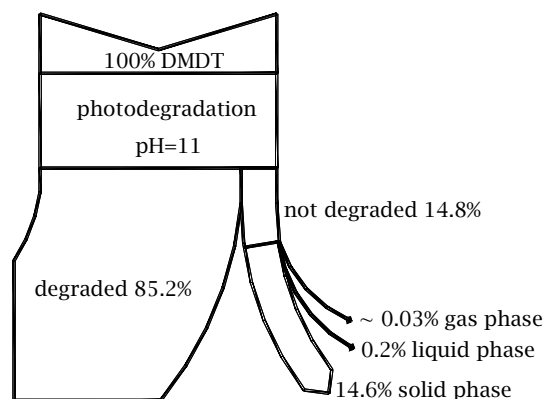


Figure 4. Sankey plot for methoxychlor photodegradation in alkaline solution, pH=11.

The byproducts of methoxychlor degradation are listed in Table 4. Adsorbed products of dechlorination were detected on the solid phase. Non-aromatic degradation products of methoxychlor were not found. Our preliminary study of chloride ion formation during 60 min. photodegradation showed, that 25 percent of chlorine atoms were abstracted from methoxychlor. In the liquid phase p-anisaldehyde, as the main degradation product, was identified (see Table 4).

4. CONCLUSIONS

Up till now the efficiency of catalytic degradation of chlorinated pesticides was analysis of the entire reaction mixture, which mean combined determination of pesticides and their degradation products in the aqueous phase and in the solid phase (catalyst). The mass balance of lindane, p,p'-DDT and methoxychlor after

catalytic photodegradation is presented here for the first time.

Although gas phase was sparged in photocatalytic reactors to enhance destruction of organic compounds, neither the original compound nor the decomposition products were detected in the gas phase leaving the process. In the experimental system used in this work the amount of lost pesticides amounted to max. 0.04%. More significant loss took place in more alkaline environment and—as expected—for pesticides with higher vapor pressure. The amount of pesticide removal with the gas phase was insignificant compared to pesticide amount introduced to the reactor, therefore it could be neglected in assessment of photodegradation efficiency.

Easily separable catalyst—TiO₂ (anatase) supported on microspheres—exhibited satisfactory degradation potential with respect to p,p'-DDT (~ 100%, pH = 11), methoxychlor (~ 85%, pH = 11) and lindane (~ 40%, pH = 11). Evaluating the results one needs keep in mind exceptionally high concentration of the pesticides (200 mg/dm³ present as fine suspension in water), relatively low intensity of the UV source, and rather short (in terms of that found in the literature) processing time.

Isomer α -HCH, pentachlorocyclohexene, tetrachlorocyclohexen, and heptachlorocyclohexane were detected as lindane degradation products—therefore chlorine atom abstraction as well as addition was observed. However, ring cleavage was not detected.

In the case of p,p'-DDT photodegradation, compounds containing from 3 to 4 Cl atoms, *i.e.*, DDD and DDE, were detected as byproducts adsorbed on the catalyst surface.

Table 4. Methoxychlor degradation products detected in the liquid and the solid phase after 60 min. irradiation.

Analyzed phase	Chemical term	CAS register number	compounds structure
liquid	p-anisaldehyde	123-11-5	
solid	benzene, 1,1'-(dichloroethenylidene) bis[4-methoxy]	2132-70-9	
	benzene, 1-methoxy-2-[2,2,2-trichloro-1-(4-methoxyphenyl)ethyl]	30667-99-3	
	benzene, 1,1'-(2,2-dichloroethylidene)bis[4-methoxy-]	7388-31-0	

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