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Photocatalytic degradation of lindane, *p*,*p*′-DDT and methoxychlor in an aqueous environment

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Abstract

Aqueous solutions containing 40 mg/dm^3 of lindane, *p*,*p*′-DDT and methoxychlor were photodegraded in a UV/TiO_2/O_2 system yielding different degradation products. Powdered anatase and rutile, and anatase supported on glass hollow microspheres served as photocatalysts. The destruction degree of pesticides was evaluated and oxidation products identified by gas chromatography with an electron capture detector (GC–ECD) and a mass spectroscopy detector (GC–MS). From 68 to 90% of pesticides investigated was eliminated after 30 min irradiation in the presence of anatase supported on glass microspheres. The lowest efficiency was obtained for rutile as a catalyst. One hundred and fifty minutes of processing resulted in 50% elimination for γ-HCH, 85% for DDT and over 99% for methoxychlor. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Lindane; *p*,*p*′-DDT; Methoxychlor; Photodegradation; Anatase; Rutile; TiO_2; Glass microspheres

1. Introduction

Advanced methods are in demand for effective treatment of pesticide-polluted ground and surface waters. Semiconductor-assisted photocatalysis has been found supplementary and complementary to conventional approaches aimed at destruction or transformation of hazardous chemical waste such as high temperature incineration, activated sludge digestion, anaerobic digestion, and physio-chemical treatment [1].

Lindane, *p*,*p*′-DDT and methoxychlor belong to most persistent pesticides in the environment. Although application of some chloroorganic insecticides in agriculture was banned in most countries in the last 20 years, thousands of tons of obsolete pesticide deposits in farms and tombs jeopardise the environment [2–4].

Heterogeneous photocatalysis using TiO_2 is regarded as a promising method for the transformation of toxic and bioresistant compounds into harmless species. In 1976, Carey et al. [5] first reported the photocatalytic degradation of biphenyl and chlorobiphenyls in the presence of titanium dioxide. Since Carey’s paper, various classes of potentially hazardous compounds, including organochlorine pesticides, were successfully destroyed during TiO_2-enhanced photocatalysis [1,6–14]. The reaction exhibits favourable kinetics in the 300–360 nm UV range.

Solar photocatalytic detoxification of industrial effluent with organic loads of hundreds of mg/dm^3 proved to be effective [15]. An aqueous solution of lindane (35.9 mg/dm^3, 686 dm^3) was tested using six parabolic modules of a collector with 180 m^2 overall aperture area. After a 1-day test, approximately 84% of the chlorine bonds to the organic carbon was broken, indicating a high degree of degradation of lindane and further intermediates [15]. In less favourable latitudes the photochemical process rather requires an artificial source of UV radiation. Sabin et al. [16] investigated photooxidation of lindane and DDT in an aqueous solution with Degussa P25 titanium dioxide as a photocatalyst. Irradiation of samples (30 cm^3 of the solution with 1.0 mM substrate concentration) was carried out in a photoreactor equipped with a 450 W xenon lamp. Photodegradation of lindane and DDT followed the first-order kinetics with 0.19 and 0.28 s^{-1} rate constants, and 9.4 and 4.3 min half-lives [16].

When TiO_2 is in the form of a suspension of fine particles, the reactor has to be supplemented with an efficient solid–liquid separator. Operation of such a separator would be much more efficient for a catalyst deposited on inert support beads. In this regard, titanium dioxide was attached to hollow glass microspheres and the activity of the resulting

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easily separable catalyst was studied in photo-assisted oxidation of selected chloroorganic pesticides. The activity of powdered anatase and rutile, and anatase attached to hollow glass microspheres was compared.

2. Experimental conditions and procedures

2.1. Reagents

Literature review of 100 recent papers pertaining to photodegradation in UV/TiO_2 system indicates that 60% of authors used Degussa P25 catalyst [17]. Others used self-prepared or commercial TiO_2. In our investigation the catalyst was prepared by hydrolysis of titanium tetrachloride on the surface of hollow glass microspheres. Commercial TiO_2 was applied for activity comparison.

Anatase from Sigma and rutile from Alfa Aesar were used as powdered catalysts for photodegradation. The specific surface area was 8.6 m^2/g for anatase and 6.9 m^2/g for rutile as determined by the Brunauer–Emmett–Teller method using nitrogen and the Quantasorb apparatus [18].

An easily separable titanium photocatalyst was prepared by chemical deposition of titanium dioxide on glass microspheres [19]. The bulk density of the microspheres investigated was 0.4 g/cm^3. The percentage of TiO_2 deposited on glass microspheres was 0.1–0.5 by weight, as revealed by the complexing TiO_2/H_2O_2 colorimetric method [19].

Lindane, *p,p*′-DDT and methoxychlor (99% pure) were obtained from Sigma. An aqueous pesticide solution/suspension was prepared by direct stirring of an acetone pesticide solution into distilled water before the reaction initiation. Acetone concentration in the aqueous phase was 0.4 wt.%. Acetone is known to be resistant to degradation in reactions involving hydroxyl radical [20]. Chemical structures of the insecticides investigated are shown in Fig. 1. The percentage of chlorine in lindane, *p,p*′-DDT and methoxychlor is 73.2, 50.0 and 30.8 wt.%, respectively.

All solvents used (acetone, *n*-heksan, methanol, cyclohexanone) were of the pesticide residue grade and were the products of Merck (Darmstadt, Germany). Analytical standards of organochlorine pesticides (lindane, *p,p*′-DDT, methoxychlor, *o,p*′-DDE) were purchased from the Pesticide Analytical Standard Institute of Organic Industrial Chemistry (Warsaw, Poland) with a purity range 99.0–99.7%.

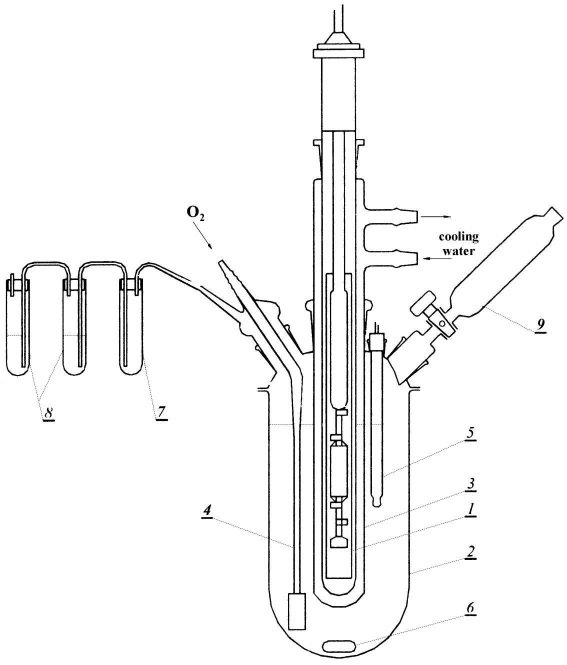
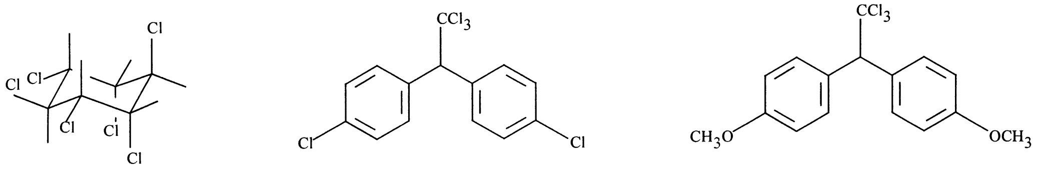


Fig. 2. Photoreactor system for pesticide destruction: (1) Heraeus medium pressure mercury lamp; (2) glass reactor; (3) UV lamp cooling system; (4) sparged gas system; (5) pH electrode; (6) stirrer; (7) drip tube; (8) absorbers for volatile compounds; (9) NaOH solution.

2.2. Irradiation experiments

A diagram showing a photoreactor used in this work is presented in Fig. 2. Pesticides dissolved/dispersed in water were photodegraded in a water-cooled laboratory UV reactor (2), equipped with a Heraeus 150 W medium pressure mercury vapour lamp (1). Half a gram of powdered titanium dioxide (as anatase or rutile) or 1 g of microspheres coated with TiO_2 was suspended in 1000 ml of an aqueous pesticide solution, which contained 40 ppm of each of the pesticides investigated. The suspension was stirred for 10 min and then irradiated in the presence of oxygen, which was sparged at the rate of 20 dm^3/h. The gas phase exiting the reactor was passed through cyclohexanone (8) to trap volatile organic compounds. The reaction environment was adjusted to pH 11 by addition of a 1 M NaOH solution.



lindane *p,p′-DDT* *methoxychlor*

Fig. 1. Chemical structure of pesticides investigated.

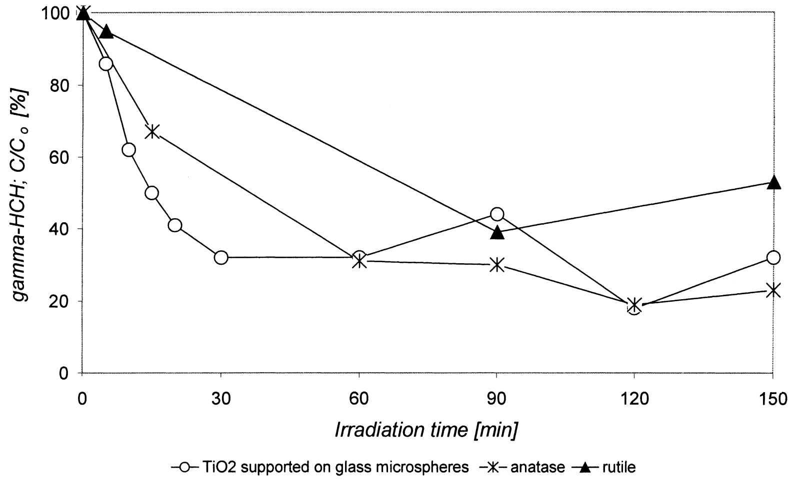


Fig. 3. Kinetics of γ-HCH photocatalytic degradation in aqueous solution in the presence of powdered TiO_2 ($0.5\,g\,l^{-1}$) and TiO_2 supported on glass microspheres ($5\,mg\,l^{-1}$) at pH 11.

2.3. Analytical procedure

Photooxidation runs were followed by the measurement of pesticide concentration by way of three analytical procedures: direct aqueous injection (DAI), liquid–liquid extraction (LLE) or solid phase microextraction (SPME) with a final analysis by gas chromatography. Internal standard (*o,p′*-DDE) was added to enhance analytical accuracy. Whilst all the methods are simple and fast, LLE yields particularly good accuracy and precision. Moreover, LLE was found appropriate for analysing a suspension since DAI and SPME were suitable only for a single-phase sample. LLE required 3 ml of aqueous samples and 1 ml of hexane, which were shaken for 3 h. Then hexane extracts were analysed by gas chromatography with an electron capture detector (GC–ECD) and a mass spectroscopy detector (GC–MS).

A Carlo Erba GC 6000 Vega 2 gas chromatograph with an ECD system, on-column injector, and RTX-5 capillary column by Restek (Crossbond 5% diphenyl–95% dimethyl polysiloxane, 30 m×0.25 mm ID, 0.25 μm film thickness) was used. The temperature program applied in the GC–ECD was as follows: 60–100°C at 30°C/min, 100–280°C at 10°C/min, 280°C (10 min). Injection was carried out in the cold-on-column mode by the injection of a 2 μl sample.

All MS measurements were performed with a Hewlett Packard HP 5971 mass-selective detector combined with an HP 5890 gas chromatograph fitted with an HP-5 capillary column (25 m×0.25 mm ID, 0.25 μm film thickness). The extracts were analysed under the same temperature conditions as when GC–ECD was applied. A split/splitless injection port and transfer line temperature were set to 250°C. A 5 μl sample was hot splitless injected with a split valve closed for 1.5 min. The MS measurements were performed with electron impact ionisation at 70 eV and in a SCAN mode. A solvent delay was set to 4 min.

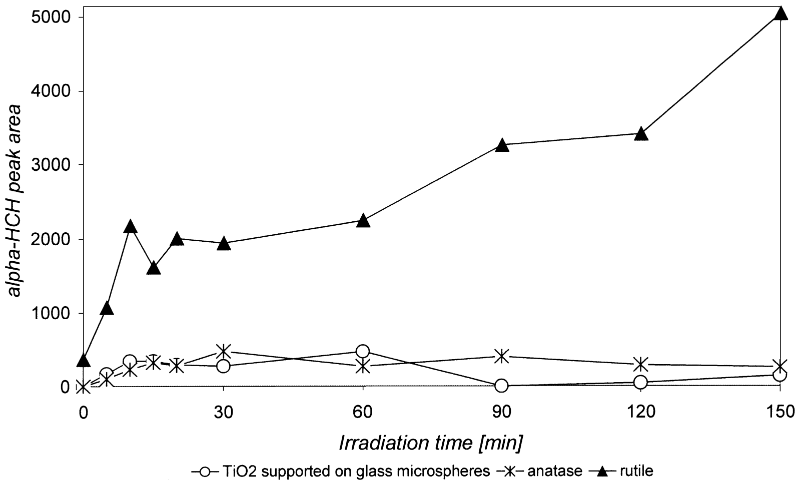


Fig. 4. Formation of α-HCH from γ-HCH during photocatalytic reaction.

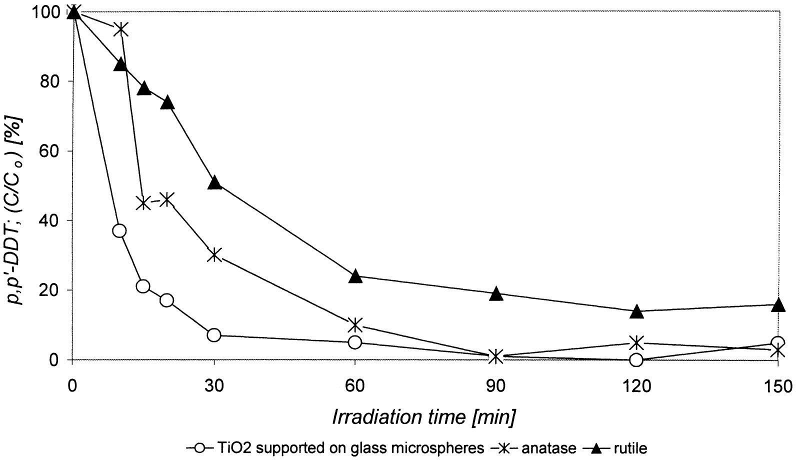


Fig. 5. Kinetics of *p,p′*-DDT photocatalytic degradation in aqueous solution in the presence of powdered TiO_2 ($0.5\,g\,l^{-1}$) and TiO_2 supported on glass microspheres ($5\,mg\,l^{-1}$) at pH 11.

3. Results and discussion

The γ-HCH degradation rate and α-HCH formation (a reaction by-product) are presented in Figs. 3 and 4. More favourable elimination kinetics was obtained for powdered anatase than for powdered rutile for all pesticides investigated (see Figs. 3, 5 and 6). The results suggest that for heterogeneous systems anatase is more photoactive than rutile, which confirms findings from the literature pertaining to other organic compounds. Palmisano et al. [21] reported that poor photoactivity of rutile resulted from almost irreversible dehydroxylation of the surface, and consequently, to the negligible capacity for O_2 adsorption.

In the presence of TiO_2 supported on glass microspheres, a rapid decrease of lindane concentration was observed at the beginning of the reaction. Thirty minutes of irradiation eliminated 68% of lindane. A much slower concentration drop was observed during subsequent 120 min of irradiation. Lindane degradation efficiency in the $TiO_2/UV/O_2$ system using powdered anatase was very close to efficiency obtained with supported titanium dioxide. Seventy seven percentage of lindane was eliminated after 150 min irradiation.

One hundred and fifty minutes of processing in the presence of powdered rutile resulted in 50% γ-HCH elimination only, however, the highest efficiency of α-HCH formation was observed in the presence of powdered rutile (Fig. 4). In the case of rutile, the amount of α-HCH formed was 100 times greater than when suspended or supported anatase was used. Exposition of γ-HCH to UV radiation results in isomerisation to α-HCH, which explains why more α-HCH was present in the reaction environment after processing when less active rutile was used.

Hiskia et al. [22] reported total photodegradation of lindane to CO_2 and HCl in a homogeneous aqueous solution in the presence of the polyoxometallate $PW_{12}O_{40}{}^{3-}$. However, the initial concentration of lindane was four times

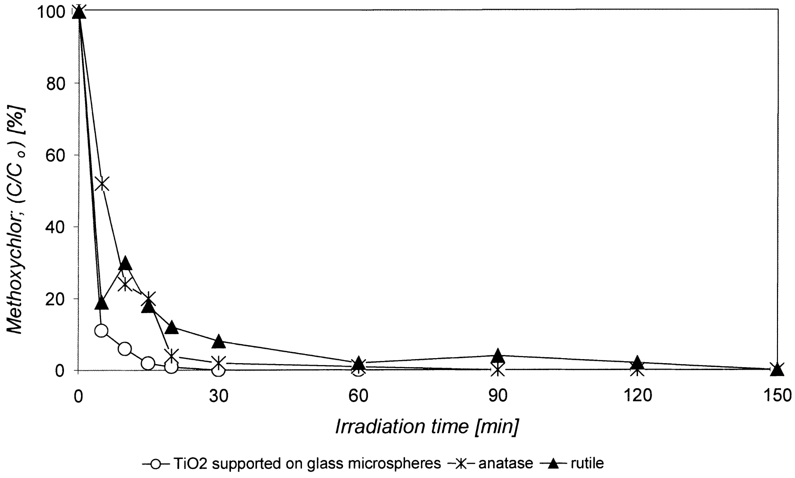


Fig. 6. Kinetics of methoxychlor photocatalytic degradation in aqueous solution in the presence of TiO_2 ($0.5\,g\,l^{-1}$) and TiO_2 supported on glass microspheres ($5\,mg\,l^{-1}$) at pH 11.

Table 1
By-products found in pesticide solution after 150 min irradiation

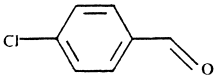
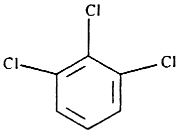
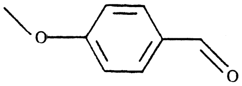
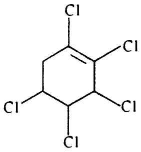
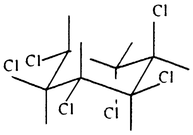
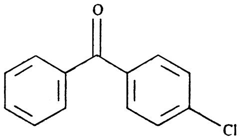
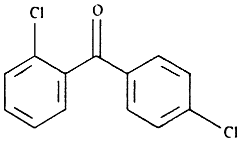
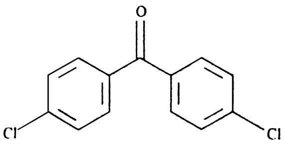
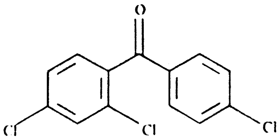
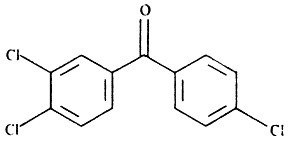
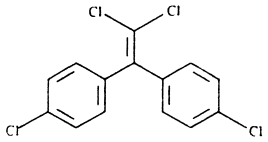
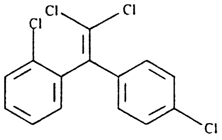
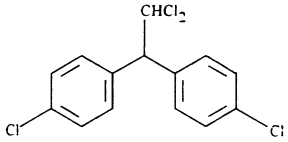
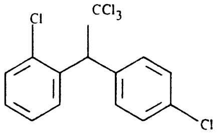
Compund's name	Retention time (min)	Parent compound	Chemical structure	Clearly present and detected	Catalyst
4-Chloro benzaldehyde	5.89	*p,p*′-DDT or DMDT		Detected	Anatase
				Detected	Rutile
				Not detected	TiO_2 supported on glass microspheres
1,2,3-Trichloro benzene	6.06	Lindane		Detected	Anatase
				Not detected	Rutile
				Detected	TiO_2 supported on glass microspheres
4-Methoxy benzaldehyde	6.53	DMDT		Detected	Anatase
				Detected	Rutile
				Detected	TiO_2 supported on glass microspheres
γ-2,3,4,5,6-Pentachloro-cyclohex-1-ene	7.48	Lindane		Detected	Anatase
				Detected	Rutile
				Detected	TiO_2 supported on glass microspheres
α-HCH	9.11	Lindane		Detected	Anatase
				Detected	Rutile
				Detected	TiO_2 supported on glass microspheres
(4-Chlorophenyl)phenyl methanone	10.01	*p,p*′-DDT		Detected	Anatase
				Detected	Rutile
				Not detected	TiO_2 supported on glass microspheres
2,4′-Dichlorodiphenyl methanone	11.40	*p,p*′-DDT		Detected	Anatase
				Not detected	Rutile
				Not detected	TiO_2 supported on glass microspheres
Bis(4-chlorophenyl) methanone	11.46	*p,p*′-DDT		Detected	Anatase
				Detected	Rutile
				Detected	TiO_2 supported on glass microspheres
2,4,4′-Trichlorodiphenyl methanone	12.18	*p,p*′-DDT		Detected	Anatase
				Not detected	Rutile
				Not detected	TiO_2 supported on glass microspheres

Table 1 (*Continued*)

Compund's name	Retention time (min)	Parent compound	Chemical structure	Clearly present and detected	Catalyst
3,4,4′-Trichloro-benzeno-phenone	12.25	*p,p*'-DDT		Detected Detected Not detected	Anatase Rutile TiO_2 supported on glass microspheres
p,p′-DDE	12.88	*p,p*′-DDT		Detected Detected Not detected	Anatase Rutile TiO_2 supported on glass microspheres
o,p′-DDE	13.17	*p,p*′-DDT		Detected Detected Not detected	Anatase Rutile TiO_2 supported on glass microspheres
p,p′-DDD	13.67	*p,p*′-DDT		Detected Detected Detected	Anatase Rutile TiO_2 supported on glass microspheres
o,p′-DDT	14.25	*p,p*′-DDT		Detected Not detected Detected	Anatase Rutile TiO_2 supported on glass microspheres

lower than in our investigation and UV radiation was much more intense, since 4 cm^3 of an aqueous lindane solution (C_0=10.8 mg/dm^3) was irradiated with a 1000 W Xe arc lamp [22]. The concentration of lindane was reduced to zero after 2–3 h of degradation and complete mineralisation of lindane occurred after 5–10 h of irradiation.

Intermediate products were identified by Guillard et al. [11] in a photocatalytically treated aqueous solution initially containing 1 g/dm^3 of lindane. The data indicate that several specified or unspecified isomers were found as the degradation products and could be classified in the following chemical categories: chlorocyclohexanes, chlorocyclohexenes, chlorobenzenes, chlorophenols, chloropropanes and chloropropanones, and the pentachlorocyclohexanone isomer [11]. The nature of by-products obtained by Guillard et al. [11] showed that chlorine and hydrogen atoms were not only abstracted from the CHCl groups constituting lindane but also added to them because heptachlorocyclohexane was also detected. In our investigation, pentachlorocyclohexen and α-HCH were identified after 150 min irradiation in the presence of each catalyst (see Table 1). Trichlorobenzene was detected after irradiation only in the presence of anatase — both powdered and supported.

After 30 min of irradiation in the presence of TiO_2 deposited on glass microspheres, the remaining *p,p*′-DDT was below 7% regarding the initial concentration (see Fig. 5). The same time of processing eliminated 70% of *p,p*′-DDT for powdered anatase. After 1 h of photodegradation in an anatase aqueous suspension, *p,p*′-DDT elimination increased to 90% and after 2 h to 95%. As in the case of lindane elimination, the lowest efficiency with respect to *p,p*′-DDT was obtained for rutile as the catalyst. Only 50% of *p,p*′-DDT disappeared after 30 min irradiation, and 85% after 150 min.

Products of DDT dechlorination, such as chlorophenylmethanone, dichlorophenylmethanone, trichloro-benzenophenone, DDE and DDD were detected after 150 min of irradiation (see Table 1). Please note that the by-products

Table 2
Rate constants for pesticide photodegradation in the presence of suspended and supported titanium dioxide

Pesticide	Rate constant k_1 (s^{-1})		
	TiO_2 supported on glass microspheres	Suspended anatase	Suspended rutile
Lindane	0.028	0.033	0.01
p,p′-DDT	0.09	0.032	0.02
Methoxychlor	0.3	0.12	0.11

were detected after photodegradation of a mixture of the three pesticides were investigated in an aqueous phase and the degradation products of *p,p′*-DDT and methoxychlor could be similar, because of a similar structure of these compounds. The degradation by-products of lindane, DDT and methoxychlor identified in this investigation and presented in Table 1 were confirmed in experimental photodegradation of single pesticides. The degradation products of 200 mg/dm^3 of individual pesticides suspended in water were reported in an earlier paper [14].

Compared to lindane and *p,p′*-DDT, methoxychlor exhibited greater susceptibility to photocatalytic degradation (see Fig. 6). After 30 min irradiation over 90% of methoxychlor was degraded in the presence of each catalyst investigated. In the case of titanium dioxide supported on glass microspheres, methoxychlor concentration was less than 10% of the initial concentration after 10 min irradiation. Only methoxybenzaldehyde was determined as the degradation product of methoxychlor after 150 min irradiation. More intermediate compounds were found after 60 min irradiation of a suspension containing 200 mg/dm^3 of methoxychlor [14]. 1,1′-(Dichloroethenylidene)-bis[4-methoxy]-benzene, 1-methoxy-2-[2,2,2-trichloro-1-(4-methoxyphenyl)ethyl]-benzene, and 1,1′-(2,2-dichloro-ethylidene)-bis[4-methoxy]-benzene were identified. Apparently these compounds were eliminated after extended processing.

Photodegradation of lindane, *p,p′*-DDT and methoxychlor in the conditions investigated followed the first-order kinetics. The rate constants are provided in Table 2.

4. Conclusions

The experimental data indicate that about 5 mg/dm^3 of titanium dioxide supported by glass microspheres provided the same elimination rate of pesticides investigated as 500 mg/dm^3 of powdered anatase. Thus it was confirmed that TiO_2 supported on the surface of glass microspheres is photocatalytically active. Moreover, this catalyst was easily separable from the reaction environment compared to powdered titanium dioxide due to low bulk density of hollow microspheres (0.4 g/cm^3).

The data confirm higher activity of anatase than rutile, a fact which is also recognised in the literature. Our data add a new group of compounds, namely chlorinated pesticides, to such observations.

Acknowledgements

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