

Dechlorination of lindane, p,p'-DDT and methoxychlor during TiO₂-enhanced photocatalysis

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Summary

Aqueous solutions containing 200 mg/dm³ of lindane, p,p'-DDT and methoxychlor were photodegraded for 60 min in UV/TiO₂/O₂ system while the chloride ions concentration and the pH changes were monitored. Titanium dioxide supported on glass microspheres, easily separable from the reaction environment, served as photocatalyst. From 38% to 99% of the investigated pesticides were eliminated after treatment. Up to 40% of chlorine atoms were split off for methoxychlor, up to 14% for p,p'-DDT, and 3% to 4% for lindane at the experimental conditions investigated.

Keywords

p,p'-DDT, methoxychlor, lindane, pesticides, photodegradation

Introduction

Organic compounds, such as chloroorganic pesticides, can be completely degraded in an aqueous environment by UV irradiation in the presence of oxygen and TiO₂-based photocatalyst [1, 2]. TiO₂-assisted photo-oxidation is usually rapid, accepts any source of 300 to 360 nm UV radiation, yields simple decomposition products and involves an inexpensive catalyst [3]. However, its application can be limited due to the difficulty of separation of the catalyst from the reaction environment. Usually, in laboratory studies, titanium dioxide powder in the form of anatase is suspended in a liquid medium [4, 5, 6, 7]. In field applications, discharge from the photo-reactor should not contain fine solids. For an easy separation, particles of the photo-catalyst should be immobilised on a fixed support or reactor wall, or the photoreactor has to be supplemented with a liquid-solid separator. The performance of the separator could be enhanced if the catalyst is deposited on easily removable and inert supporting particles such as glass beads [8].

In the present paper, earlier investigation on lindane, p,p'-DDT and methoxychlor depletion in an aqueous solution in UV/TiO₂ system (which included degradation products identification and mass balance of the photodegradation reaction) [9,10], was supplemented with considerations on formation of chloride ions.

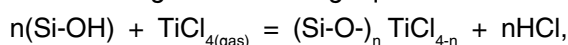
Materials and methods

Reagents

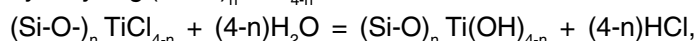
Lindane, p,p'-DDT and methoxychlor (99% pure) were obtained from Sigma Chemical Co. All solvents used (acetone, cyclohexanone) were of the pesticide residue grade and were the products of POCh (Gliwice, Poland). Analytical standards of organochlorine pesticides (lindane, p,p'-DDT, methoxychlor, o,p'-DDE) were purchased from the Pesticide Analytical Standard Institute of Organic Industrial Chemistry (Warsaw, Poland) with a purity ranged between 99.0 and 99.7%. Titanium tetrachloride was of laboratory reagent quality supplied by POCh (Gliwice, Poland).

Preparation of catalyst

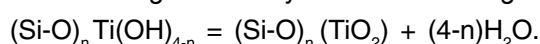
Titanium dioxide was deposited on glass microspheres by exposing the microspheres to titanium tetrachloride vapour according to the following equation:



hydrolysing $(\text{Si-O})_n \text{TiCl}_{4-n}$:



and calcining titanium hydroxide at 500 deg C to titanium dioxide [11]:



SEM images of a glass micro-sphere prior to treatment and of titanium dioxide immobilised at the surface of a glass micro-sphere are shown in Figures 1 and 2 [12]. The complexing $\text{TiO}_2/\text{H}_2\text{O}_2$ colorimetric method revealed that 0.1 to 0.5 wt % of TiO_2 was deposited on the glass micro-spheres. X-ray diffraction analysis showed that the titanium dioxide immobilised at the microsphere surface was of the anatase form, i.e. more active form of titanium dioxide in photocatalytic degradation.

Micro-spheres float on the water surface due to their low bulk density (0.4 g/cm^3). In this regard, the catalyst would be easily separable after reaction by skimming. The chemical composition of glass micro-spheres poses no environmental threat [13].

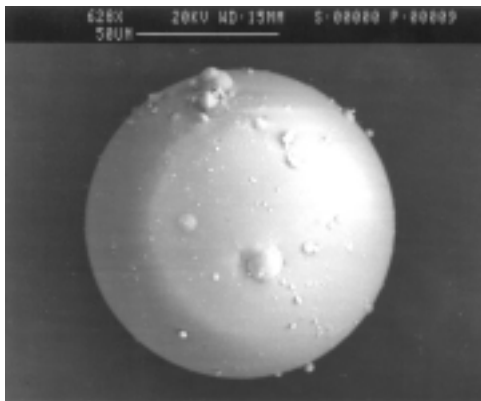


Figure 1. Glass microsphere recovered from coal-fired power plant fly ash

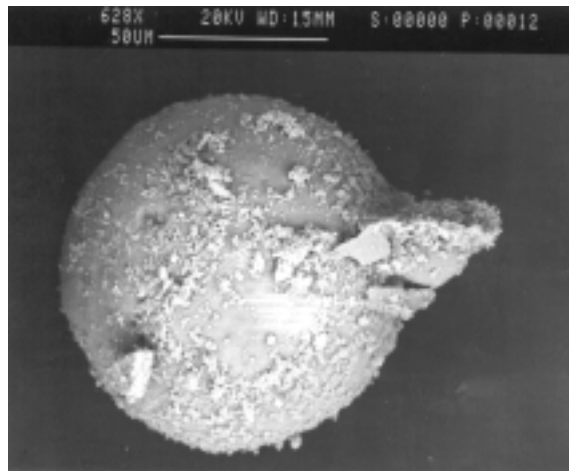


Figure 2. Glass microsphere coated with titanium

Irradiation procedure

Degradation tests of lindane, p,p'-DDT and methoxychlor were carried out using Heraeus laboratory UV reactor equipped with 150 W medium pressure mercury lamp in presence of oxygen, air and argon. All gases were sparged at $20 \text{ dm}^3/\text{h}$ rate (see Figure 3). 1 g of glass microspheres coated with TiO_2 served as photocatalyst. 1,100 ml of aqueous suspension containing 200 mg/dm^3 of each of the mentioned pesticides was irradiated for 60 minutes. Pesticide aqueous solution/suspension was prepared by blending acetone pesticide solution with distilled water. The aqueous phase was continuously stirred (3) during irradiation and gas sparging. The gas phase leaving photo-reactor was sparged through cyclo-hexanone (7) to trap volatile organic compounds. Chlorine ions concentration and the pH were measured each 5 minutes using Hydromet ECI-01 ion-selective electrode (9), Hydromet RL-100 reference electrode (10), and Hydromet glass combined electrode (11).

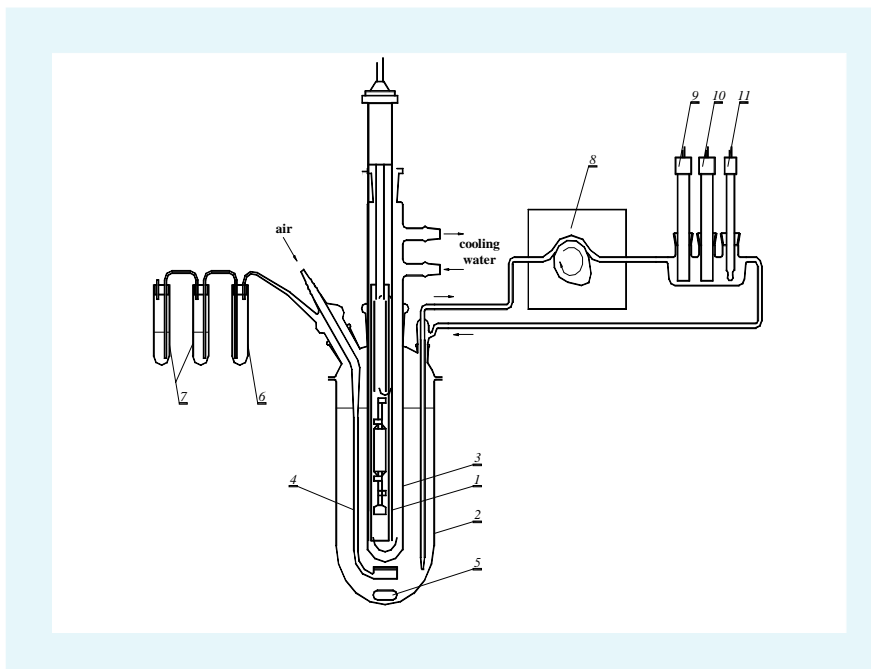
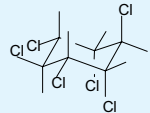
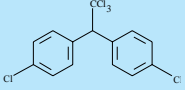
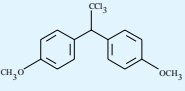


Figure 3. Schematic diagram of photoreactor for pesticide destruction with *-on line-* measurement of Cl^- and H^+ ions concentration: 1-Heraeus medium pressure mercury lamp, 2- glass reactor, 3- UV lamp cooling system, 4- gas sparger, 5- stirrer, 6- drip tube, 7- absorber for volatile compounds, 8- peristaltic pump, 9- ion-selective electrode, 10- reference electrode, 11- pH electrode

Results and discussion

The chemical structure of lindane, p,p'-DDT and methoxychlor, and pesticides elimination effect for an aqueous solution/suspension containing 200 mg/dm³ of the investigated compounds in the presence of TiO₂ supported on glass microspheres are shown in Table 1. Chlorine makes 73.2 wt. %, 50.0 wt. % and 30.8 wt. % in each molecule, respectively. After 60 minutes, irradiation of lindane eliminated only about 40 % of the compound. The same reaction time resulted in 60.3 % elimination of p,p'-DDT in unbuffered solution and in 99.2 % elimination in buffered alkaline environment [9]. Insignificant difference in methoxychlor degradation efficiency was observed for both investigated pH values. The experimental results (Table 1), indicated that methoxychlor was eliminated from 80 to 85 percent.

Table 1. Degradation of lindane, p,p'-DDT and methoxychlor after 60 minutes irradiation in 200 mg/dm³ aqueous suspension

Compound	Chemical structure	Elimination of parent compound in the presence of air [%]		Chloride ions formation [%]		
		pH=6	pH=11	Ar	Air	O ₂
Lindane		38.5	41.2	3	3	4
p,p'-DDT		60.3	99.2	8	10	14
DMDT		80.5	85.1	4	27	40

Assuming complete dechlorination of 200 mg/dm³ pesticide, the concentration of chloride ions should amount to 146.4 mg/dm³ for lindane, 100.1 mg/dm³ for p,p'-DDT, and 61.6 mg/dm³ for DMDT. From 3% to 40% chlorine atoms present in the pesticides were transformed to chloride ions after 60 minutes exposure (Figures 4-6). Compared to lindane and p,p'-DDT, methoxychlor exhibited greater susceptibility to dechlorination during photocatalytic reaction.

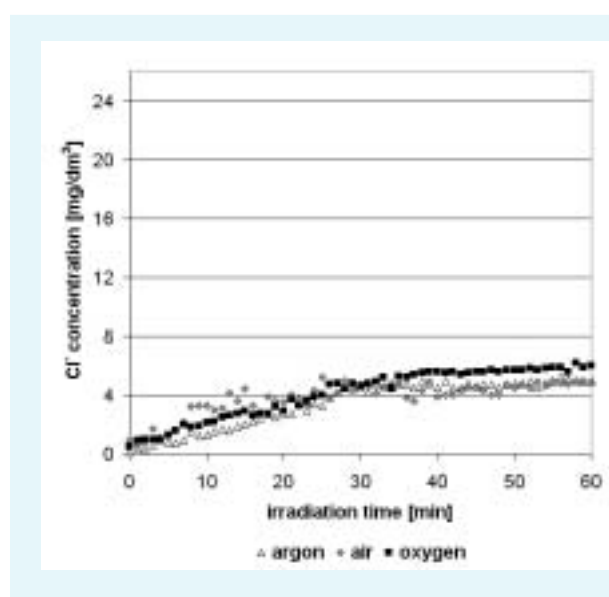


Figure 4. Chloride ions formation during photodegradation of aqueous suspension containing 200 mg/dm³ of lindane, gas flow rate 20 dm³/h, TiO₂ supported on glass microspheres

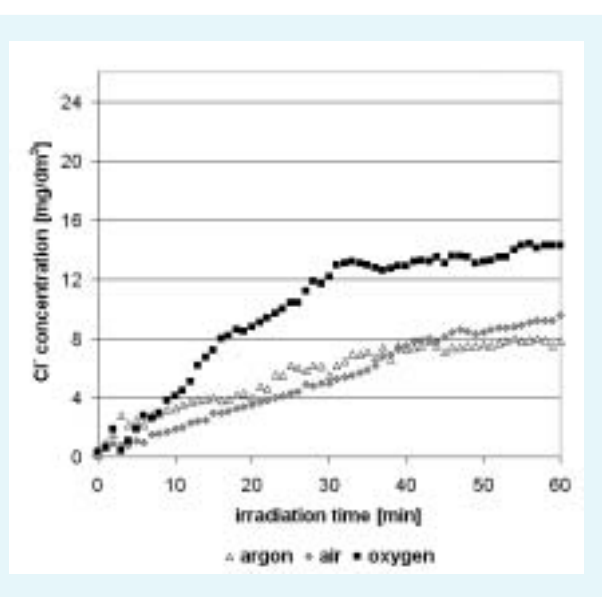


Figure 5. Chloride ions formation during photodegradation of aqueous suspension containing 200 mg/dm³ of p,p'-DDT, gas flow rate 20 dm³/h, TiO₂ supported on glass microspheres

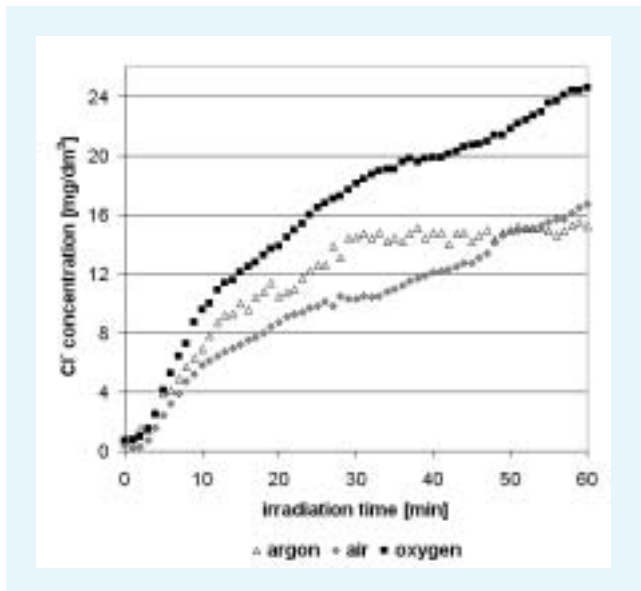


Figure 6. Chloride ions formation during photodegradation of aqueous suspension containing 200 mg/dm³ of DMDT, gas flow rate 20 dm³/h, TiO₂ supported on glass microspheres

The lowest efficiency of dechlorination was observed for lindane (Table 1, Figure 4).

After 60 minutes irradiation, chloride ions concentration was about 5.0 mg/dm³ for argon, 5.0 mg/dm³ for air and 5.9 mg/dm³ for oxygen, which corresponds to 3%, 3% and 4%. Only for lindane the dechlorination rate was independent on oxygen concentration in the reaction environment. The pH value dropped to 3.4.

After 60 minutes irradiation, Cl⁻ concentration for p,p'-DDT reached 7.6 mg/dm³ in the presence of sparged argon, 9.6 mg/dm³ in the presence of air, and 14.3 mg/dm³ in the presence of oxygen. It makes 8%, 10% and 14% of the theoretical value, respectively (Table 1 and Figure 5). During the first 40 minutes of irradiation, no difference in the chloride ion concentration for argon and air was observed. It might indicate that residual oxygen was still present in the reaction environment despite of the 10 minutes argon purging prior to irradiation. This effect was observed in the case of methoxychlor. The pH value dropped to 3.4 [13].

Processing of 200 mg/dm³ of methoxychlor for 60 minutes resulted in the following concentration of chlorides: 15.1 mg/dm³ for argon, 16.7 mg/dm³ for air, and 24.6 mg/dm³ for oxygen, which corresponds to 24%, 27% and 40% of the theoretical value (Table 1 and Figure 6). 60 minutes irradiation dropped the pH from 6.3 to 3.1.

Conclusions

The concentration of chloride ions confirmed earlier chromatographic data [9] that after 60 minutes irradiation in the presence of titanium dioxide the investigated chloroorganic pesticides underwent partial oxidation and HCl was present among the decomposition products.

Compared to lindane, p,p'-DDT and methoxychlor exhibited greater susceptibility to photocatalytic degradation. p,p'-DDT was eliminated up to 99% and methoxychlor was eliminated up to 85% in an alkaline solution (pH=11).

Photodegradation of p,p'-DDT and methoxychlor is dependent on the presence of oxygen in the reaction environment. Oxygen purging into the reactor increased dechlorination efficiency of methoxychlor almost three times compared to purging argon.

Acknowledgement

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