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Heterogeneuos Photocatalytic Degradation of Hazardous Waste in Aqueous Suspension

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ABSTRACT

The photocatalytic degradation of hazardous waste like chlorinated paraffin compound (1,12-Dichlorododecane Dcd) was investigated in different aquatic media using GC-MSD. The direct photolysis of Dcd in HPLC water was considered to be negligible (k = 0.0020 +- 0.0007 h^{-1}). An acceleration of the photodegradation rate was occurred in presence of different TiO_2 catalyst systems. Molecular oxygen was found to play a vital role in the degradation process. Anatase TiO_2 was proved to be the most efficient one (k = 0.7670 +- 0.0876 h^{-1}), while the rate constant of the rutile TiO_2 was calculated to be 0.2780 +- 0.0342 h^{-1}. Improvement of photocatalytic efficiency of rutile TiO_2 was achieved by addition of Fe^{+2} giving a rate constant = 0.6710 +- 0.0786 h^{-1}.

***Key Words:** Photodegradation, Catalysts, 1,12-Dichlorododecane.*

INTRODUCTION

One of the famous classes of industrial organochlorine compounds is the chlorinated paraffins (Cps) group. The short-chain chlorinated paraffins (carbon chain length C_{10} - C_{13}) are considered to be the most important class of this group as they have the greatest potential for environmental release (1). Cps are produced and consumed in large scale globally, and are considered to be highly toxic compounds(2-4). Cps do not undergo direct photolysis, but may degrade when exposed to light in the presence of oxidizing radicals (5) and are completely destroyed at 300 to 400 °C (6,1).

In the past decade, the applications of semiconductors for photocatalyzed oxidation of aqueous pollutants has been very helpful for water purification(7). An important advantage of photocatalytic processes is that they may be performed at low or ambient temperatures and that complete mineralization of the organic compounds may be achieved (8).

Although the photoactivity of TiO_2 has attracted a great deal of attention, few studies have focused on the influence of the different phases and structures of titanium oxide. In contrast to anatase phase TiO_2, which has been commonly used from commercially available sources as a successful photocatalyst, rutile phase TiO_2 has been reported to be a very poor photocatalyst.This is attributed to its higher hole-electron recombination rate (9, 10). However, Sclafani et al. (11), examined several commercial and prepared TiO_2 samples and found that the activity of rutile was influenced by its preparation conditions.

The objective of this work was to study the rate of photodegradation of 1,12-dichlorododecane (Dcd) in pure HPLC water and in presence of different TiO_2 catalyst systems. The effect of dissolved O_2 was also investigated.

EXPERIMENTAL

1. CHEMICALS

1,12- Dichlorododecane (98%) and titanium dioxide (anatase and rutile) were purchased from Aldrich Chemical Co. (Milwaukee, WI). Ferrous ammonium sulphate was purchased from Fisher Scientific, (Edmonton, AB).

All solvents used were of GC, HPLC and spectrophotometry grade. HPLC water used for sample preparation was Burdick & Jackson Brand High Purity and was purchased from VWR Scientific of Canada Ltd. (Mississauga, Ontario). Acetone, Methanol, Hexane and Acetonitrile were purchased from VWR Scientific of Canada Ltd. (Mississauga, Ontario).

2. INSTRUMENTATION

Quantitative analyses of 1,12-Dichlorododecane were carried out with a Hewlett Packard (HP) 5890 GC coupled to a HP 5970 MSD using the selected-ion-monitoring (SIM) mode. The column used was a 30 m x 0.25 mm x 0.25 mm (Supelco SPB-5). A 1 ml sample was injected via a HP 7673 autosampler into a splitless injection port held at 200 °C. Helium was used as carrier gas. A typical temperature program was as follows: initial temperature held at 75 °C (1 min), 25 °C/min to 200 °C, 10 °C/min to 225 °C, then 25 °C/min to 280 °C (9.5 min).

UV spectral analysis was carried out using Hewlett Packard 8452A Diode Array Spectrophotometer.

3. KINETICS OF PHOTOLYSIS

Photolysis of 1,12-Dichlorododecane was carried out in tightly capped 50-mL Pyrex centrifuge tubes. A control blank sample of the same composition as the sample under study was used for each experimental set. The control blank tube was wrapped with aluminum foil to prevent photolysis.

A stock solution of 1,12-dichlorododecane was prepared in 1:1 acetonitrile/ water. A specific volume this solution was added to each sample, in which the concentration of Dcd was adjusted to be 8.38 0.33 µg/L. Acetonitrile content was kept constant at 0.0004 v/v in each of the different samples und investigation.

The photodegradation rate of Dcd was studied in the following aquatic media: a) pure HPLC water, l HPLC water saturated with highly purified O_2, c) anatase TiO_2 suspended in O_2 saturated HPLC wate d) rutile TiO_2 suspended in O_2 saturated HPLC water, e) rutile TiO_2 suspended in O_2 saturated HPL water in presence of 1mM Fe^{+2}, f) rutile TiO_2 suspended in N_2 saturated HPLC water in presence (1mM Fe^{+2}.

For the above preparation, oxygen or nitrogen flow rate of 15 mL/min was allowed to pass for 3 minutes before irradiation, 1% w/v anatase or rutile TiO_2 was used.

A 150 watt Xenon lamp was used as a light source to simulate the sunlight spectrum. This lamp emi radiation from 290 nm and through the visible region of the emission spectrum. Kinetic data we determined in duplicate and averaged for each time interval.

Extractions of Dcd from water were performed using C-18 Sep-Pak cartridges. Refreshment of each Sep Pak was carried out by passing 5 mL hexane, 5 mL acetone, 5 mL methanol, respectively followed by 1 mL HPLC water through each prior to extraction. Recovery of Dcd from the Sep-Pak was achieved usin 10 mL hexane. The extracts were dried by passing through them anhydrous Na_2SO_4 (dried at 300°C backed column, and concentrated to 1 mL, using a gentle stream of highly purified N_2 prior to analyses.

RESULTS, DISCUSSION AND CONCLUSION

1. PHOTOLYSIS IN HPLC WATER

Figure 1 represents the UV absorption spectrum of 1,12-dichlorododecane (Dcd) in 1:1 HPL(water / acetonitrile solution. The spectrum shows a broad, tailing band with maximum absorbance a 254 nm and a cut-off at 280 nm. Since no absorption occurs above 290 nm, Dcd will not underg direct photolysis under sunlight or simulated sunlight conditions.

As shown in Table 1, the rate constant of photodegradation of Dcd in pure HPLC water was calculate to be 0.0020 ± 0.0007 h^{-1}. This indicates that, direct photolysis of Dcd is considered to be negligibl which is obviously clear from the UV spectrum analysis.

Quantitative recoveries of the parent Dcd from dark controls over the entire exposure period indicate negligible losses due to biological and chemical degradation, volatilization, and/or analytical procedures.

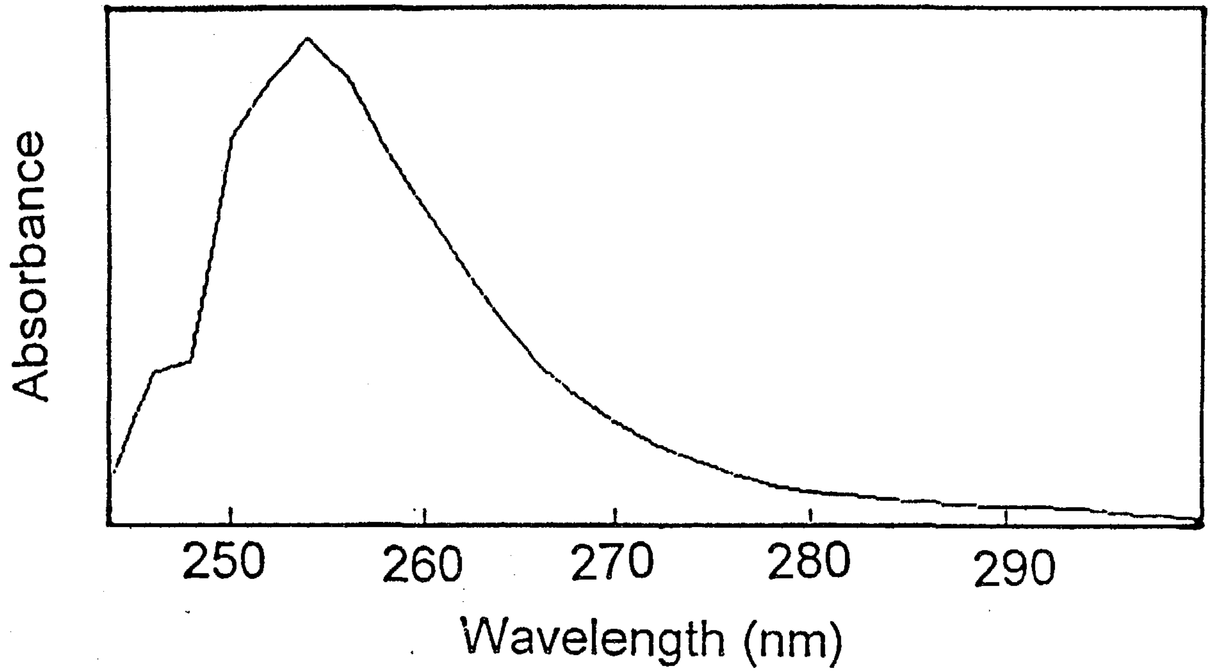

Figure 1. The absorption spectrum of 1,12-dichlorododecane in 1:1 acetonitrile/water

Table 1: Pseudo first order rate constants and half-lives of photodegradation of 1,12-dichlorododecane under different conditions.

Reaction medium	k (h^{-1})*	$t_{1/2}$ (h)
HPLC water	0.0020 ± 0.0007	346.5
O_2	0.2710 ± 0.0165 a	2.6
anatase TiO_2/O_2	0.7670 ± 0.0876 a	0.9
rutile $TiO_2/N_2/Fe^{+2}$	0.0030 ± 0.0006 bc	231.0
rutile TiO_2/O_2	0.2780 ± 0.0342 a	2.5
rutile $TiO_2/O_2/Fe^{+2}$	0.6710 ± 0.0786 ac	1.0

*Pseudo-first order rate constants measured in different aquatic media, ^{a}HPLC water saturated b bubbling O_2 for 30 minutes with a flow rate of 15 mL/min before irradiation, ^{b} HPLC water saturated b bubbling N_2 for 30 minutes with a flow rate 15 mL/min before irradiation, ^{c} In presence of 1 mM ferrou ammonium sulphate.

2. PHTOLYSIS USING DIFFERENT CATALYST SYSTEMS

The photoexcitation of TiO_2 semiconductor particles by near-UV results in the transition of electron from the valence band (vb) to the conduction band (cb) generating (e^-) - hole (h^+) pairs$^{(8)}$, (Equation 1)

$$TiO_2 + h\nu \longrightarrow e^-_{cb} + h^+_{vb} \qquad (1)$$

As noted earlier, in n-type semiconductor, e.g. TiO_2, the more reactive species are the holes, which carr the major part of the energy of the light spectrum. The holes may react by recombination with electror (lowering the quantum efficiency), or may react with organic molecules (Equation 2), or with surfac $OH^-_{ads}$$^{(8)}$ (Equation 3).

$$h^+ + RH_2 \longrightarrow RH^{\cdot} + H^+ \qquad (2)$$

$$h^+ + OH^-_{ads} \longrightarrow OH^{\cdot} \qquad (3)$$

Since, holes at the particle interface react faster than electrons, the particle under illumination wi contain an excess electrons. Removal of these excess electrons is necessary to complete the oxidatio reaction of an organic compound, Preventing the recombination of electrons and holes. The most obtaine easily and economic electron acceptor is molecular O_2 (Equation 4).

$$e^- + O_2 \longrightarrow O^{-}_{2} \qquad (4)$$

Although Dcd does not degrade by direct photolysis in HPLC water, the rate of degradation was found to be enhanced by saturation with molecular O_2 (Table 1 and Figure 2). A significant increase of the photodegradation rate is observed in the presence of anatase TiO_2 and saturation with O_2. Anatase TiO_2 is considered a good photocatalyst in presence or absence of O_2 (12; 13), or in presence of dissolved metal ions (14), or even in presence of low concentration of H_2O_2 in the range of 10^{-4} to 10^{-2} M (15).

The increased rate of the photodegradation of Dcd in presence of O_2 or anatase TiO_2 saturated with O_2 reveals that molecular O_2 plays the main role controlling the rate and mechanism of the photoreaction. In the presence of molecular oxygen the negatively charged electrons, produced from the photoexcitation of TiO_2, are preferentially trapped by oxygen, forming either super oxide anion radicals, Equation 4, or hydrogen peroxide, Equation 5, which leads to the production of hydroxyl radicals, Equation 6, (7).

$$2e + O_2 + 2H^+ \text{ --------> } H_2O_2 \qquad (5)$$

$$O^{\cdot}_2 + H_2O_2 \text{ --------> } OH^- + OH^{\cdot} + O_2 \qquad (6)$$

The influence of dissolved O_2, N_2 and Fe^{+2} on the photodegradation of Dcd in the presence of rutile TiO_2 was also studied (Figure 3). The rate constant in presence of rutile TiO_2 saturated with O_2 was calculated to be $0.2780 \pm 0.0342\ h^{-1}$, similar to the rate constant obtained using HPLC water saturated with O_2 ($0.2710 \pm 0.0165\ h^{-1}$, Table 1). This suggests that rutile TiO_2 has no considerable effect in the degradation of Dcd.

Comparing the rate constants of the photodegradation in presence of TiO_2 saturated with O_2 in its two different phases, the rate was found to be 3-fold faster in presence of anatase.

In N_2 saturated rutile TiO_2 suspension in the presence of Fe^{+2} ions, the rate was considered to be negligible ($k = 0.0030 \pm 0.0006\ h^{-1}$, $t_{1/2} = 231$ h). However, addition of Fe^{+2} ions in O_2 saturated TiO_2 rutile suspension caused a significant decrease of Dcd half-life (from 231.0 h to 1.0 h). Again, the presence of molecular oxygen with TiO_2, anatase or rutile, assists the photodegradation process.

It is to be noted also that in the presence of Fe^{+2}, the reaction between holes and Fe^{+2} is supposed to be the most probable (Equation 7) decreasing the recombination between holes and electrons on the rutile surface. This step probably occurs in a relatively fast step, whereas, the rate limiting step may be transfer of the photoexcited electrons to molecular O_2. Formation of $O^{\cdot}_2$ leads to the production of $OH^{\cdot}$ radicals which react readily with Dcd molecules forming organic radical species. By further oxidation complete mineralization is believed to occur to the organic radical species.

$$h^+ + Fe^{+2} \text{ --------> } Fe^{+3} \qquad (7)$$

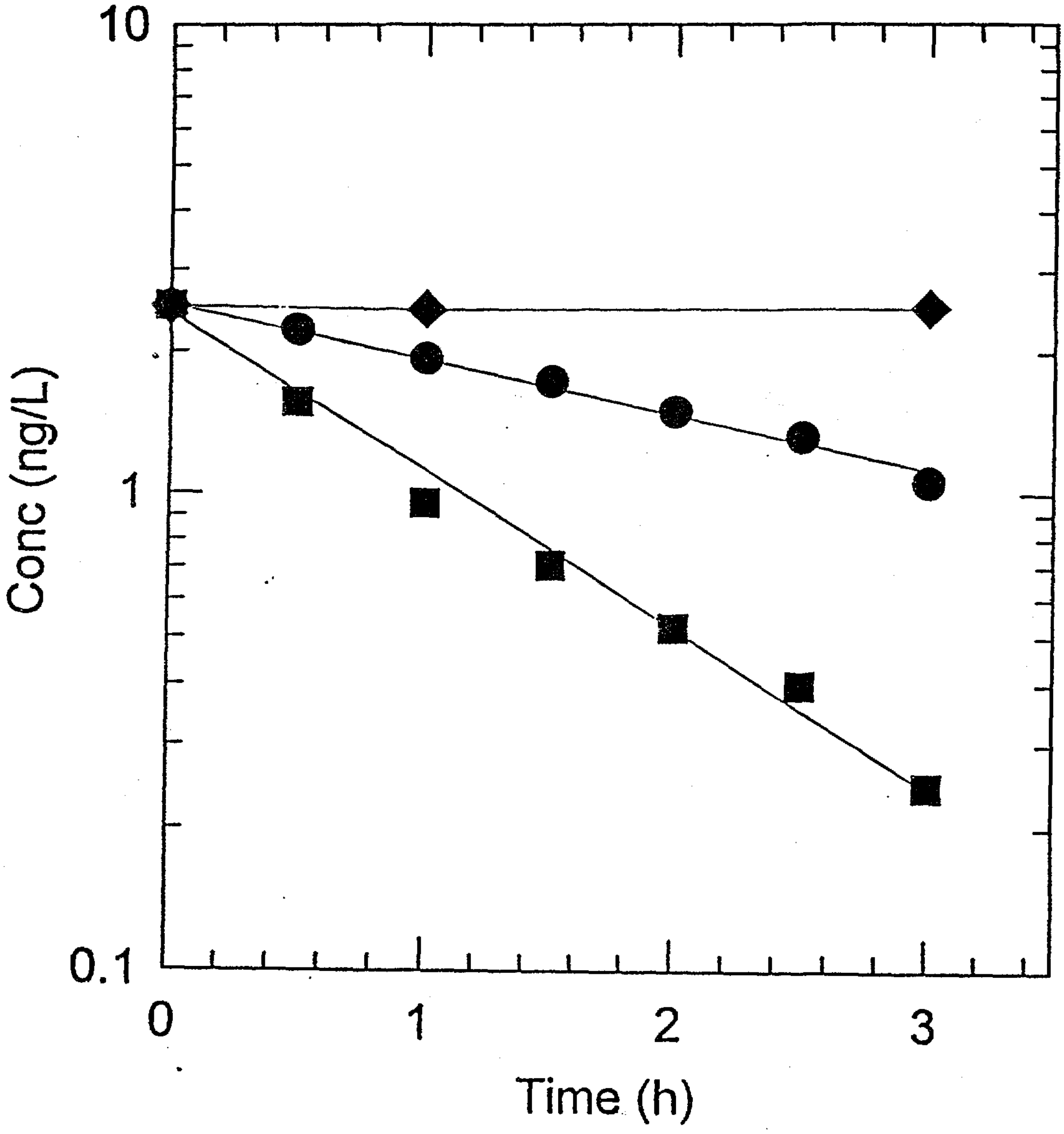

Figure 2. Photodegradation of 1,12-dichlorododecane in, (◆) HPLC water, (●) HPLC water saturated with oxygen, and (■) HPLC water saturated with O_2 in presence of 1% w/v anatase TiO_2. The data representing the degradation of Dcd with n=2 ateach time interval

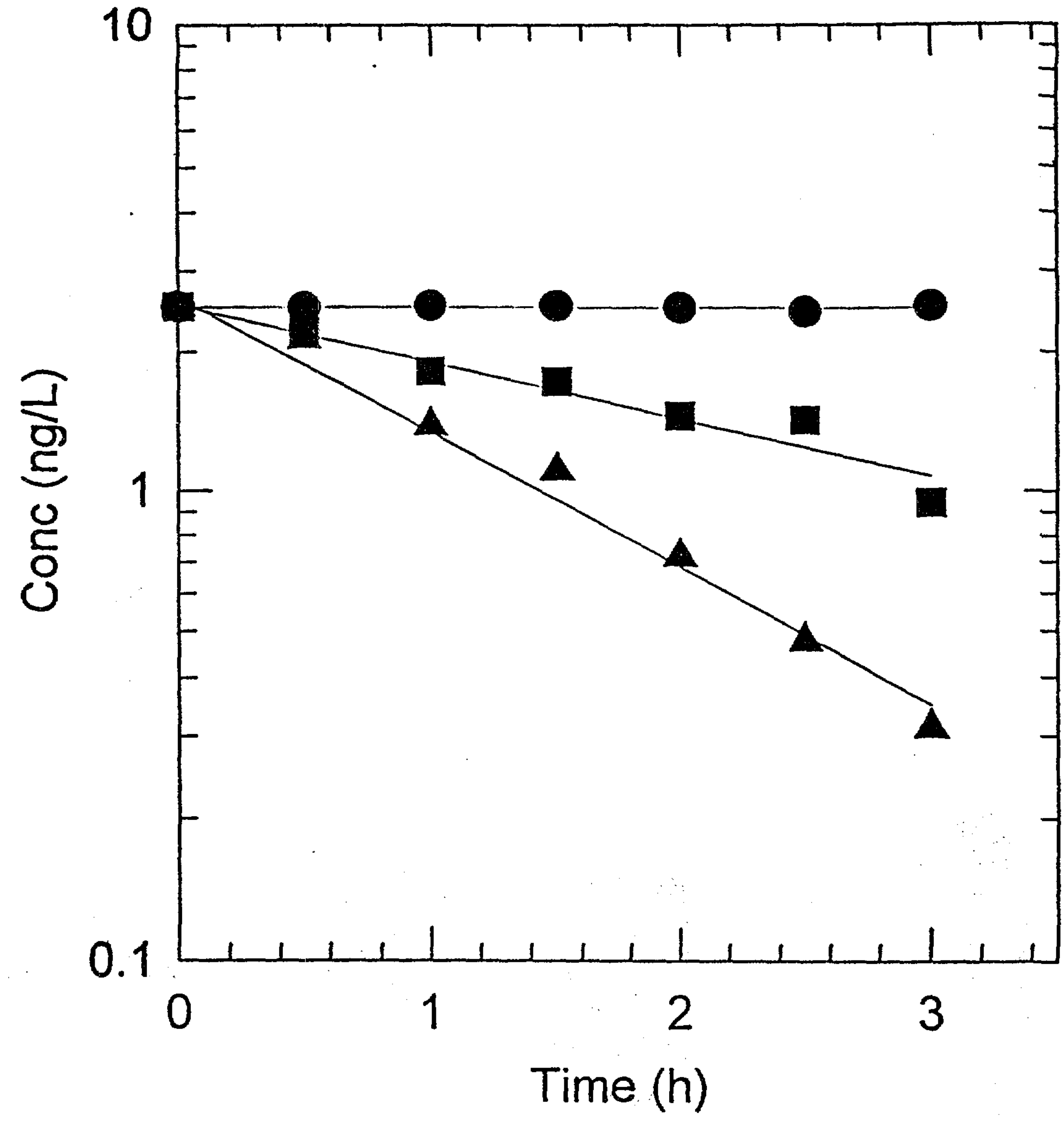

Figure 3. Photodegradation of 1,12-dichlorododecane in, (●) HPLC water saturated with N_2 in presence of 1% w/v rutile TiO_2 and 1 mM Fe^{+2}, (■) HPLC water saturated with O_2 in presence of 1% w/v rutile TiO_2, and (▲) HPLC water saturated with O_2 in presence of 1% w/v rutile TiO_2 and 1mM Fe^{+2}. The data representing the degradation of Dcd with n=2 at each time interval

CONCLUSION

From the obtained results one may conclude that, Dcd could not be degrade at all in pure HPLC wate (very slow $t_{1/2} = 346.5$ h). Homogeneous photodegradation in presence of dissolved O_2 was found to b very helpful. Heterogeneous Photodegradation in presence of different TiO_2 catalyst systems indicate that anatase TiO_2 is the most efficient one. However, improvement of photocatalytic efficiency of rutil TiO_2 was achieved by addition of Fe^{+2} ions. The order of photodegradation rates of Dcd in differen aquatic media are; $UV/O_2/TiO_2$ anatase > $UV/O_2/Fe^{+2}/TiO_2$ rutile > $UV/O_2/TiO_2$ rutile $\simeq$ UV/O_2.

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