Kinetic Study of 2,4,5- Trichlorophenol Photodegredation in the Presence of TiO_2

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Abstract

The effects of non- porous powder samples of TiO2 (with specific surface areas of about 55 m^{2}g-^{l}) on the kinetics of disappearance of 2,4,5Trichlorophenol (2,4,5- TCP) in water were determined.

The photocatalytic character of the 2,4,5- TCP disappearance in its presence was shown by (i) the effects of the catalyst mass on the initial rate r_o, (ii) the Langmuirian -type relationship between r_o and Co (iii) the low activation energy of 2,4,5- TCP disappearance (iV) the effect of pH solution, (V) the effect of initial concentration Co of 2,4,5- TCP on the rate of photodegradation r_o by using medium pressure mercury lamp at 125 W.

الخلاصة

تم خلال البحث الحالي دراسة الاكسدة الضوئية المحفزه لمركب 2 ، 4 ، 5 – ثلاثي كلوروفينول باستخدام اوكسيد التيتانيوم ذو مساحة سطحية حوالي 55م^2 .غم وجد ان سرعة عمليات الاكسدة الضوئية تتاثر كثيراً بالعوامل التالية (1) تاثير كمية TiO_2 على السرعة الابتدائية r_o(2) علاقة لانكاير بين r_o و (3) C_0 القيمة الواطئة لطاقة التنشيط لاختفاء 2 ، 4، 5 – ثلاثي كلورفينول (4) تاثير pH المحلول (5) تاثير التركيز الابتدائي لـ 2 ، 4 ، 5- ثلاثي كلورفينول باستخدام مصباح زئبقي متوسط الضغط بقدرة 125 واط.

Introduction

The presence of chlorinated aromatic pesticides in the environment represents a very serious problem because of their toxicity, persistence and their widespread utilization(I.2).

The degradation of these compounds is possible through chemical, photochemical, and biological process(I), but most of these methods require long treatment periods and are difficult to apply in' practical disposal attempts.

For instance, the photochemical degradation of these chlorinated aromatics has been reported by several investigators(3). In natural waters the presence of dispersions of humic acids seems to contribute, together with light and oxygen, to their decomposition. The most common reactions observed when chlorinated organic contamil1ants are irradiated with ultra- violet light are dechlorination, substitution of chlorine atoms by hydroxyl groups, and formation of radical species(3). In some cases, exposing chlorinated phenols to sunlight has led to the fonl1ation of products which may be more toxic than the original pollution substance(4).

Barbeni and coworkers(5) studied the sunlight photo degradation of 2,4,5- trichlorophenoxyacetic acid (2,4,5- T) and 2,4,S-chlorophenol (2,4,5- TCP) in oxygenated aqueous suspensions of $Ti0_2$. Gas-chromatographic! mass spectrometric evidence has led to indentification of several intermediate species. These are indicated in the degradation of the 2,4,5- T; the primary major species is the 2,4,5- TCP.

Experimental details

Material:

$Ti0_2$ was Degussa P-25 grade (mainly anatase, non-porous, 50 m^2 g-I). 2,4,5- Trichlorophenol was obtained from Aldrich (purity greater than 99%) and was used as received. A Milli-Q water Purification system (Millipore) provided the water used for all solutions and suspensions .

Photoreactor and light source

The UV- light is generated from (125 W) medium pressure mercury lamp supplied from OSRAM (Germany). The Photolysis experiments were carried out in t11e photolysis Pyrex cell (35 cm^3). A magnetic stirrer was used to keep the solution in homogeneous suspension through the photolysis process.

Oxygen gas was passed with rate of 10 cm^3/ min. The UV -Visible spectra were recorded with double beam cintra- 5 spectrophotometer.

The incident light intensity was measured by the well known ferrioxalateactinometry (6) .The average light intensity between 300-365 nm (medium pressure mercury lamp) is 9.3 x 10-^{8} Einstein L-^{1} S-I.

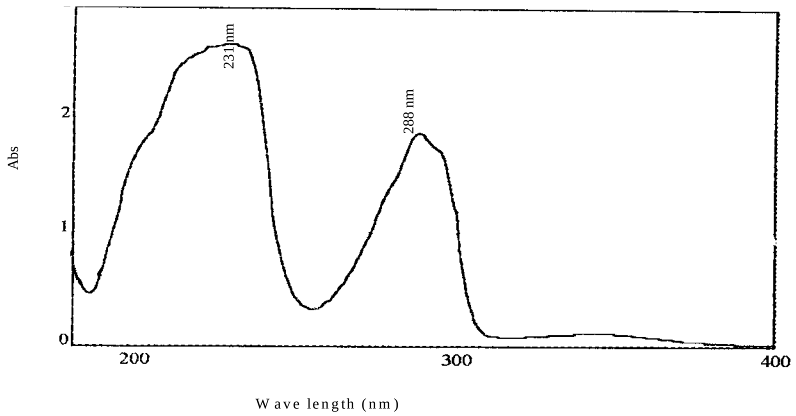
Photodegradation Experiments

All photodegradatio experi ments were carried out by irradiation the aqueous suspension of 2,4,5-Trichlorophenol by UV-Visible light emitted from medium pressure mercury lamp MPML in the reaction vessel fitted with quartz window with reaction vessel fitted with quartz window with continuous stirring of suspension and bubbling of oxygen by using compressor, the suspensions were irradiated for 75 min. A small quantity (0.5 ml) of suspension filtrated to remove TiO_2. In the presents work , the photodegradation for 2,4,5- Trichlorophenol solution in presence of sensitized $Ti0_2$ as photocatalyst were also carried out under sunlight exposure for (8 hrs) during the summer day in 2001.

was taken and centerfugated and .

The aqueous solution of 2,4,5-Trichlorophenol (10-^{2} M) shows two maximum absorption bands at 231 nm and 288 nm, that the absorption always decrease in . intensity with irradiation time leading to practically no absorption bands in the UV-visible region (200-400nm) as shown in figure (I).

Result and discussion



Fig(1): UV.-visible absorption spectrum of (2,4,5-TCP] in aqueous solution (1x 10^{-2} mol L^{-1}), pH = 1, 298K.

Effect of solar radiation without Ti0$_2$

The reaction vessel was exposed to the UV radiation without Ti0$_2$ for 3 hr. It \vas noticed that 2,4,5Trichlorophenol is quite stable under solar condition this mearl that light, O$_2$ and Ti0$_2$ are very essential for photocatalytic degradation of 2,4,5-Trichlorophenol $^{(7)}$.

Effect of Ti0$_2$

A series of experiment have been done by Llsing different weights of TiO!2 in presence of O$_2$ ancllight at 298 K.

Figs (2) and (3) show that the unrate of induced photodegradation of [2,4,5- TCP] always increases, with increasing Ti0$_2$ loading until it reaches a plateau behavior at a .. concentration of[4.8 g/L].

At this, value the rate of degradation levels off and remain constant up to 6 g L-' after this value of rate was decreased because it did not absorbed the light by the particles LL1 the suspension for :example.

In the present work the value [4.8g/L] of added Ti0$_2$ was considered to be the optimum loading of Ti0$_2$ for each initial taken during photolysis experiments

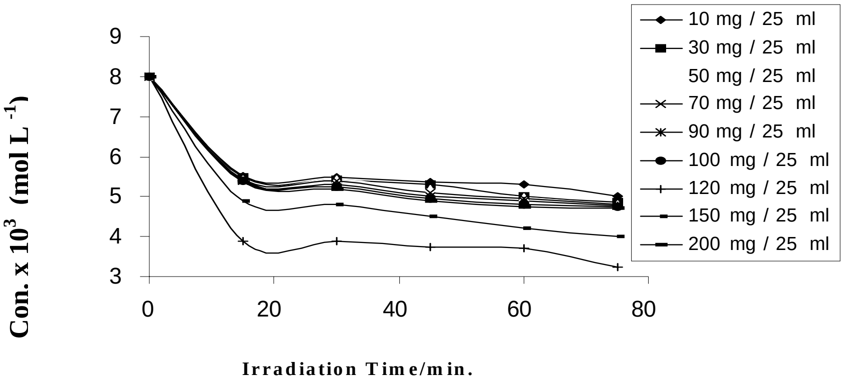


Fig. (2): Relation between the concentration of 2,4,5-trichlorophenol and irradiation time at different TiO$_2$ loading 0.12g/25 ml. At pH= 1, T= 298 K and C$_o$ = (1x10^{-2}M).

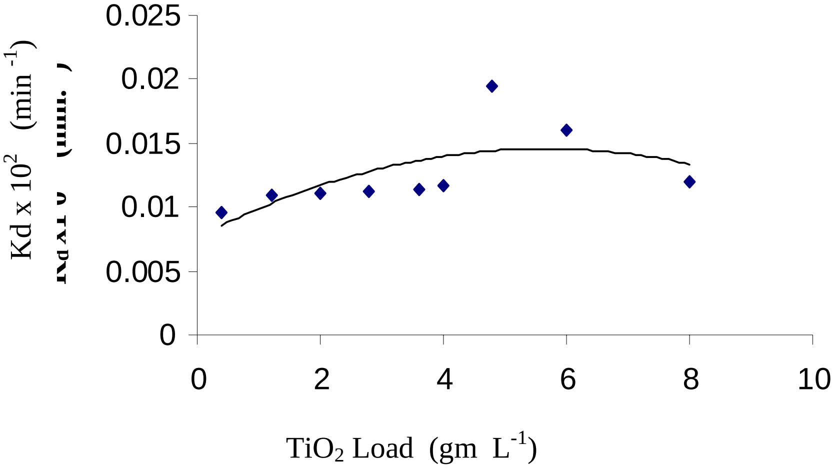


Fig.(3): The relation between the rate of photodegradiation and TiO_2 load. At pH = 1, T= 298 K and C_o = (1x10^{-2}M), TiO_2 = 0.12 g/ 25 ml.

Effect of temperature and determination the activation energy(E_a)

The photocatalytic degradation .. reaction of 2,4,5- Trichloro phenol [2,4,5- TCP] have been carried out by varying the reaction temperature from [283-303]K.

Table (1) presents the specific rate constant (k:!) for [2,4,5- TCP] photo decomposition in aqueous anatase suspension at different temperatures.

Table (1): Temperature effect on the pecific rate constant of the photodegradation of2,4,5- Trichloro phenol [2,4,5- TCP] [lxtO-^{3} mole L-^{1}] in aqueous *TiG_2* suspension [4.8 gel] at 10 ml min-^{I} oxygen flow rate~ Naked *TiG_2*.

Temperature °K	283	288	298	298	303
Specific Rate constant K_d×10^{4} sec $^{-1}$	0.98	1.43	1.82	2.16	3.06

Temperature has been proved to be an important parameter when studying the photcatalysis of chlorophenols .

Ridah and and coworkers (8) found that the oxidation rate of 2CP did not change significantly in the range of (15 to 65) °C. Chen and Ni(9) reported that the rate increases according to the following equation:

$$\log k_{\mathrm{d}} = \frac{-\Delta E}{2.303\,R} \cdot \frac{1}{T} \;\ldots\ldots(1)$$

Y= -2.0102× + 3.1048

R^2=0.9811

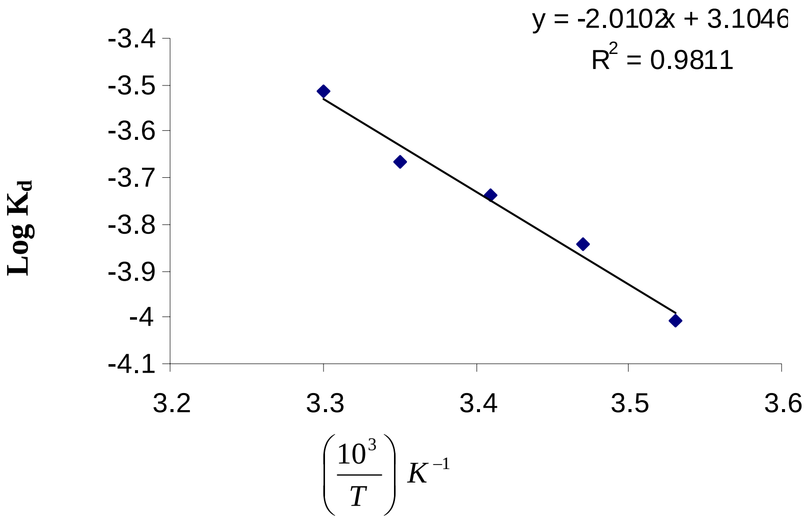


Fig. (4): Arrehenius plot of 2,4,5-TCP in naked TiO_2 . At pH= 1, T = 298 K and $C_o = (1x10^{-2}$ M) and 0.12 g /25mL TiO_2.

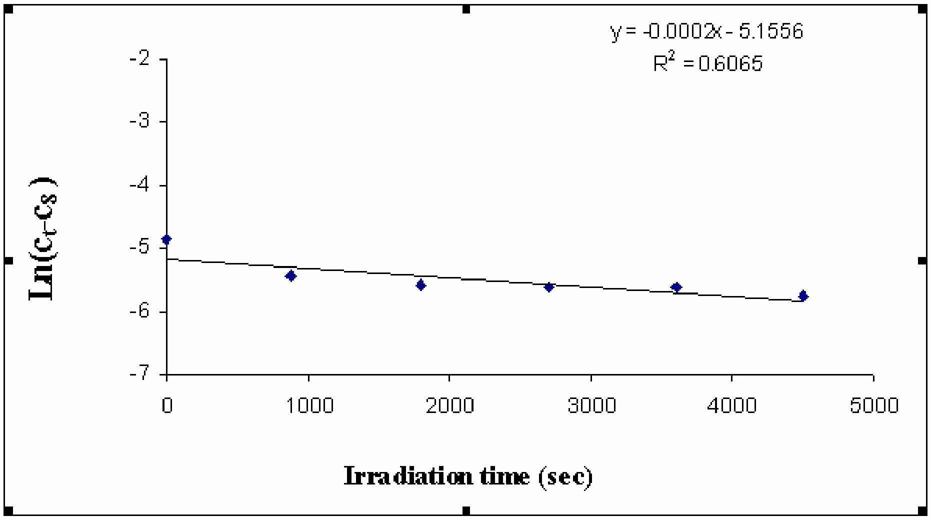


Fig. (5): Relation between $\ln(C_t - C_\infty)$ with irradiation time to the 2,4,5-TCP in presence of TiO_2 (4.8 g mL^{-1}) . At pH= 1, T= 298 K and $C_o = (1x10^{-2}$ M).

Effect of initial concentration of 2,4,5- Tri chlorophenol on the rate of photodegradatioll reaction

In a given photocatalyst loading, the rate is increased therefore in the present work, the .. plot of initial (2,4,5-TCP) concentration vs. irradiation time is shown in Fig. (6). Fig.(7) illustrates that the initial rate constant decreases as the initial concentration increase until it reaches a plateau value at the initial concentration of 8 x 10^{-2} mol L^{-1}.

Furtheremore $^{(9)}$ the relation between the reciprocal reaction rate (l/r) and reciprocal of the initial concentration (l/[CoD is linear as shown in Figure(7). This is also in consistent with the linearity from of the Langmuir Hinshel wood equation $\frac{I}{r} = \frac{I}{K} + 1/Kk[C_0]$ as has been found in· many other investigations From the intercept and slope of Fig.(7) the specific rate constant (k) for and [2,4,5TCPl has beeri calculated, which is equal to 1.965 x 10^{-4} sec^{-l} and 60.975 Sec^{-l} respectively .

Table (2) illustrates the initial 2,4,5- Trichlorophenol [2,4,5- TCPl concentrations, specific rate constant k_J, half-lives measured and calculated rate of [2,4,5- TCPl photodegradation measured and calculated rate of [2,4,5- TCPl photoclegradation. The results in table (2) SllOWS a good agreement between the measured and calculated values of the rate values.

Table (2): The initial rate of 2,4,5- Tri chlorophenol disappearance at various initial concentration Co when TiO_2 loading is 4.8 gm L^{-1} and initial pH is I.

C0 mole. L_{-1} × 10_2	Kd sec^{-1} × 10^4	$T_{1/2}$ min	Observed rate 10^5 r_o^a	Clculated rate × 10^5 r_o^b
2	3.82	78.141	0.764	0.7272
4	3.05	22.721	1.22	1.4546
6	2064	26.25	1.58	1.9677
8	2.26	30.663	1.8	2.5008
18	1.94	35.721	3.88	2.9863

r_o^a Average of 5 runs at theae initial concentrations

r_o^b By use of the aquoted values of k_d and K an the Langmiur- Hishel wood relationship

These are in agreement with the result reported by Koster and coworkers$^{(8)}$ for the photo catalytic degradation of.. chlorobenzen. AI-Ekabi and Serpone $^{(10)}$ have also found that this behavior could be related to the saturation effect of chlorophenols compounds; they also found that this behavior could be related to the saturation effect of chlorophenols compounds adsorbed on the TiO_2 surface.

Also Al - Sayyed and coworkers $^{(11)}$ show the similar behavior and results. May workers have studied the effect of the cases, it was found that an increase in the concentration of contaminate involves a decrease in the photo catalytic reaction rate . A plausible explanation can be that: when the initial concentration increases more organic substances are adsorbed on the surface of TiO_2, but the intensity of light and illumination time LS constant, consequently the OH radical concerned is' formed. On the surface of TiO_2 is constant, the relative number of OH radicals attacking the chlorphenols decreases and thus the photodegradation efficincy decreases too.

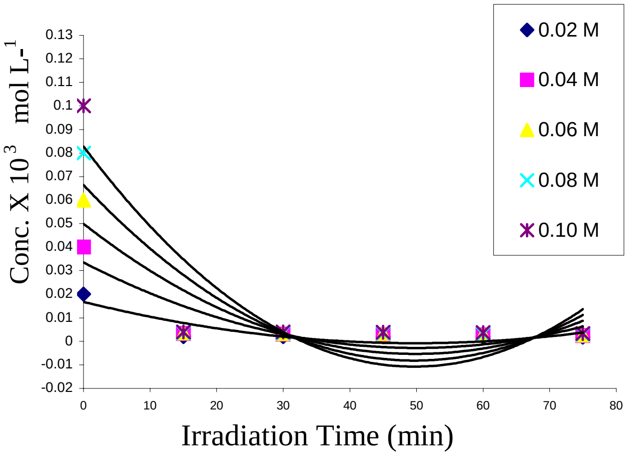


Fig. (6): The effect of variation of initial concentration of (2,4,5-TCP) with irradiation time. At T= 298 K and 0.12 g / 25 mL TiO_2 solution.

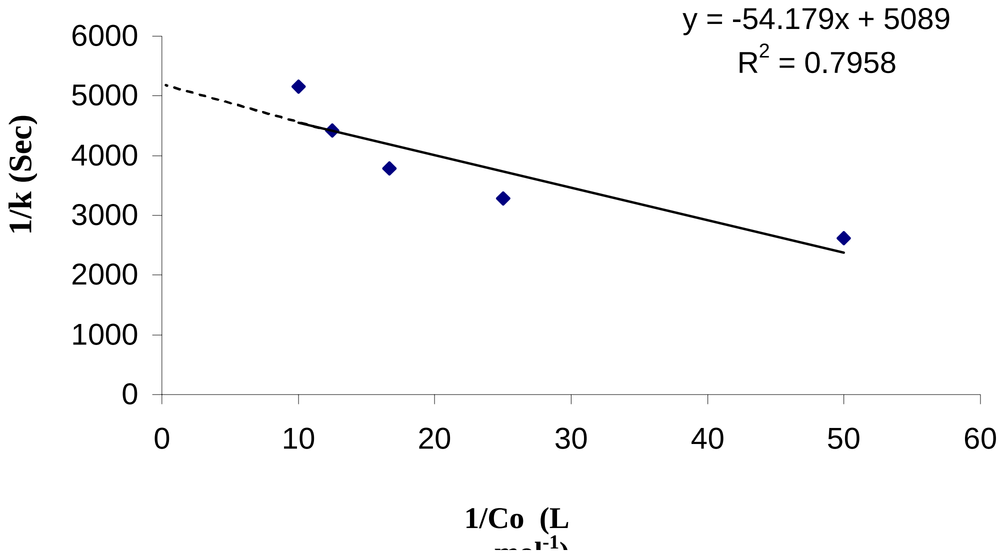


Fig. (7): Plot of reverse of the initial concentration of 2,4,5-TCP disappearance in TiO_2 aqueous (4.8 g mL^{-1}) . At, T= 298 K against reciprocal of the initial concentration.

Chan and coworkers (12) and Rideh and Coworkers(7) observed that an increase in the initial concentration of 2- chloro phenol when degraded photo catalytically by TiO_2 involved a decrease in the rate of degradation. Chen and coworkers (13) studied the photocatalytic degradation of 2-chlorophenol 2,4,-Dichlocatalytic and 2,4,6- TCP in the presence of manganese ions at pH =3 by varying the concentration of the chlorophenol in all the cases the rate constant (k_d) of the photo degradation decreases when increasing the initial concentration of the chlorophenols .

The pH of the aqueous solution significantly affects the particle size, the surface charge, and the band edge positions of the $Ti0_2$ due to it's amphoter character . The zero point charge (pHzpc) or pH at which the surface of an oxide is uncharged for $Ti0_2$ is around 7. Above and· below this value, the catalyst is negatively or positively charged according to equation [1 and 2].

In consequence the photocatalytic degradation of organic compounds is affected by the pH (14.15).

TiOH2 + <=> TiOH + H+ [acidic] ……..(2)

TiOH <=> TiO- + H+ [basic] …………...(3)

The photocatalytic degradation process of [2,4,5TCP] has been carried out in different solution of pH ranged from pH 4 to pH 9 as in fig (8). The highest photodegradation rate was achievied when pH is equal to 4.

Table (3) shows the initial rate of [2,4,5- TCP] photocatalytic oxidative degradation process in different solution of pH.

All other parameters were kept constant. The rate of photocatalytic degradation of 2,4,5-TCP on $Ti0_2$ surface was also determined in the solution pH ranged from 4 to 9

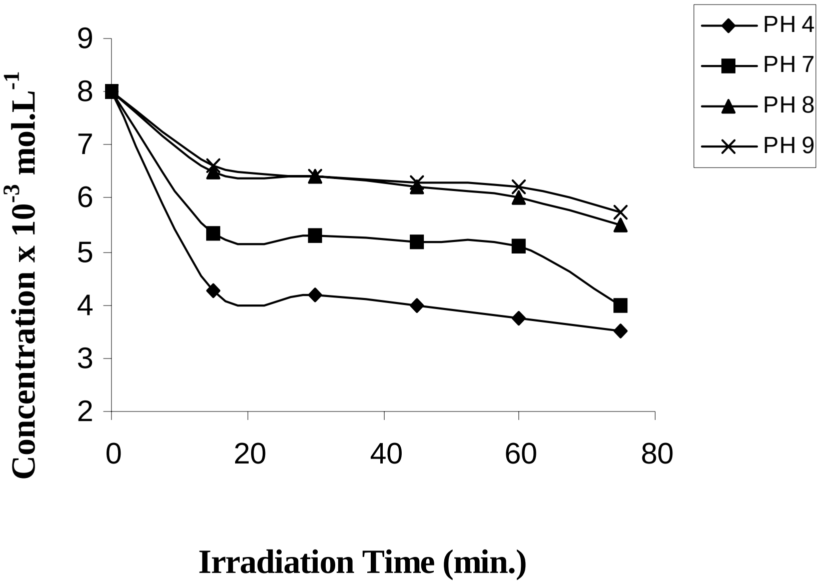


Fig. (8): Effect of pH on the rate of photo degradation of (2,4,5-TCP) .At pH= 1, T= 298 K and $C_o = (1x10^{-2}M)$.

Table (3): the specific rate constant K_d of [2,4,5- TCP] degradation at various pH values, when the initial [2,4,5- TCP] concentration is 1 x 10-^{3} mole L-^{t} , Oxygen now rate is 10 mL min-^{I} and 298 K.

pH	k_d x 10 ^{4} sec $^{-I}$
4	2.23
7	1.43
8	0.82
9	0.71

The pH value has a great effect on the photodegration efficiency of chlorophenols. The report in Literaure (14 -16) suggest that Ti0$_2$ surface carries a positive change at low pH value while the CPs [chloro phenols] and intermecl iates are primarily negatively and neutrally charged. Therefore, low pH values can facil itate the ·adsorption of the organic molecule and promote better photo catalytic degradation.

This result is in agreement with the results obtained by Ku and coworkers(17), where the photo deoradation of 2- chlorophenol [2-CP] in the presence of Ti0$_2$ under various pH solution showed higher pseudo-first order photo catalytic rate constant at pH=3.

However, better removal efficiency of CPs in Ti0$_2$ IUV system under alkali condition has also been reported (.16.18.19). One possible explanation is that the photo catalytic transformation of chloro phenol [CPs] does not involve hydroxyl radical oxidation exclusively and direct electron transfer and surface sorption reaction also contribute significantly to the disappearance of CPs in the Ti0$_2$ suspensions (18).

Another possible explanation is that Ti0$_2$ has an amphoteric character with a zero point charge around pH = 6 (20), and the substrate can undergo acid -base equilibrium .

Consequently, the adsorption of the substrate may be affected, strongly influencing the deoradation rate (21). The results presented by Doong and Coworkers (22) and Riden and coworkers (7) show that the rate constant is lower in acidic medium than in basic medium for the photo degradation of 2-CP in the presence of Ti0$_2$. Tang and Huang (23) studied the photo degradation of 2,4-Dichloro ophenol and found that the optimum pH for this system was 5 .

Salah and Abdul-Kadir have studied the effect of pH solution on the photo degradation of some pesticides (24). The highest photo activity has been found at pH equal to 5.

Experiments with higher pH than 9 and 'lower than 5 could not be conducted and the optimum conditions (e.g.Ti0$_2$ load, particle size and OJ flow rate) were

applied. These results are in good agreement with that reported by Kormarn and coworkers(21).

HPLC cllrolllatograpllic analyses (25)

High performance liquid chromotography IS a suitable technique for analysis for 2,4,5-trichlorophenol [2,4,5- TCP] Ll1 aqueous medium. Fig. (9) shows the HpLC chromotogram for 2,4,5- trichlorophenol [2,4,5- TCP] in aqueous material before irradiation, and after 30,60,90,120min, irradiation .

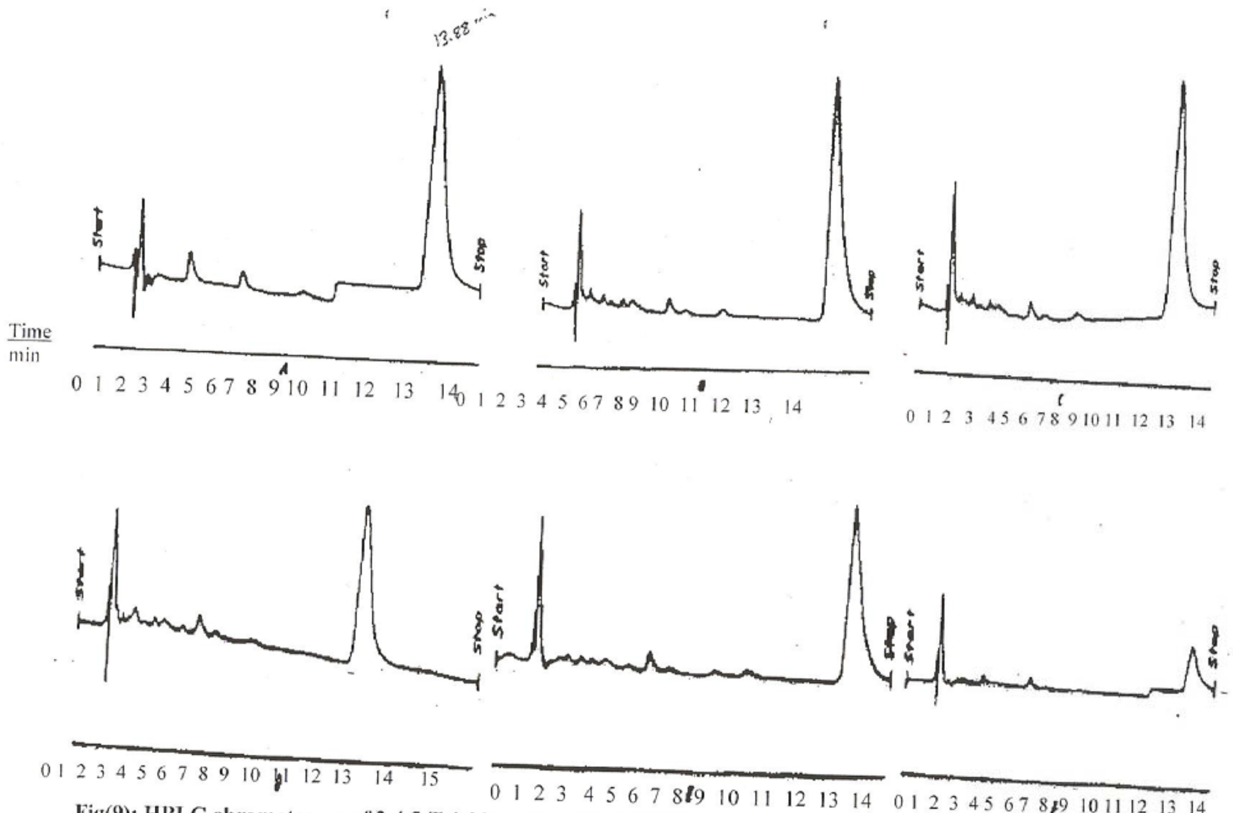
absorbance peak appeared at retention time of 13.88 min and after irradiation the intensity of this peak is gradually decreased with irradiation time.

A new absorbance peaks starts to appear after 60min and this is located at 3.89min [this peaks did not appear clearly because of the low concentration of 2,4,5 – TCP]

Test analysis of authentic compounds were revealed that this

new peak was related to hydroquinone or catichole [R_t = 3.89 or 3.87 minutes]. After 3hours of irradiation the 2,4,5TCP peak continue to decrease and also the primary product peak [R(= 3.89 minutes] starts to Irradiation time of 12 hours show that no HPLC peaks were detected [using optimum initial concentration of 2,4,5- TCP [2 x 10^{-2}mole L^{-1}]

These results are in a good agreement with that obtained for the UV.- visible spectral changers results in Fig.(9), and that again proves that the primary photolytic product is Hydroquinone or catichol which in turn is photomineralized to inorganic species.



Fig(9): HPLC chromatogrm of 2,4,5-Trichlorophenol [2,4,5-TCP] Solution [(A) before photolysis (B) after 30 min (C) after 60 min (D) after 90 min (E) after 120 min] irradiation. Initial [2,4,5-TCP] concentration is 1x 10^{-3} mol L^{-1}. TiO_2 loading is 4.8 gm L^{-1} and oxygen flow rate 10 ml. min^{-1}. The HPLC operating conditions are: mobile phase methanol: water (65: 35 V/V) Column 25 cm x 4.6 mm C_{18} and UV. Detector.

Mechanism of Reaction

Barbeni and coworkers (5) studied the photocatalytic degradation of 2,4,5-trichloro phenoxy acetic acid and 2,4,5- trichloro phenol in oxygenated aqueous suspensions of $Ti0_2$. Complete mineralization to CO_2 and HCl occurs.

In the degradation of the 2,4,5- Trichloro phenoxy acetic acid several intermediates were

detected by gas - chromatographic / mass - spectrometric techniques.

When chlorinated organic contaminates are irradiated with ultra - violet light, the most common reactions observed are dechloroination, substation of chlorine atoms by hydroxyl groups and the formation of radical species.

In some cases exposing chlorinated phenols to sunlight has led to the formation of products which may be more toxic than the original pollution substance. The problem was that no intermediate could be observed by the various techniques owing to the rapid degradation process. Gas chrometographic / mass - spectrometric evidence has led to identification of several intermediate .

These are indicated in the degradation of the 2,4,5- TCP; the primary major species is the [2,4,5- TCP]. The amount of Cl^- and CO_2 formed quantitatively confirms the complete mineralization bf 2,4,5- TCP gave 1.2 x 10^{-5} moles of CO_2, occurding to the soichiometric equation (4) (I).

$$\left[HOC_6H_2Cl_3 + \frac{11}{2}O_2 \xrightarrow{hV} 6CO_2 + 3HCl .... (3) \right]$$

According to their results the degradation of 2,4,5- TCP induced by irradiated $Ti0_2$ dispersions show a particular behavior compared to chlorophenol investigated earlier (I)

In fact it was possible to identify several interesting intennedes during the photodegradation by GTc/Ms technique-Scheme [1] summarizes the intermediation observed and identified after 20min of irradiation time.

The intermediate species were detected in a wide range of concentration, which allowed to propose the several degradation pathways illustrated in Scheme [2].

The identification of different intermediates is dependent on the stability of the intermediate itself as some of these species . undergo further fast oxidation 2,4,5- TCP(III) and 2,4,5- Trichloro phenol formate (IV) are the two major and longer lived intermediate

products of the photo degradation of 2,4,5- T.

$$TiO_2 \xrightarrow{hV} e^- cb + h^+ vb. \qquad ....(5)$$

$$H_2O + h^+ vb \rightarrow {}^0OH + H^+ \qquad ....(6)$$

$$H^+ + e^- cb \rightarrow {}^0H \qquad ....(7)$$

$$O_2 + e^- \rightarrow O_2^{0-} \xrightarrow{H^+} HO^0 2 \qquad ....(8)$$

$$2HO^0 2 \rightarrow O_2 + H_2O_2 \xrightarrow{O_2^0} {}^0OH + {}^-OH + O_2 ...(9)$$

where the subcripts (C_b) and (V b) represent conduction and valence band, respectively. The 'OH [and HO·2] radicals can subsequently undergo a series of reactions with the 2,4,5- T, leading to the products summarized in the scheme illustrated in the Scheme [2].

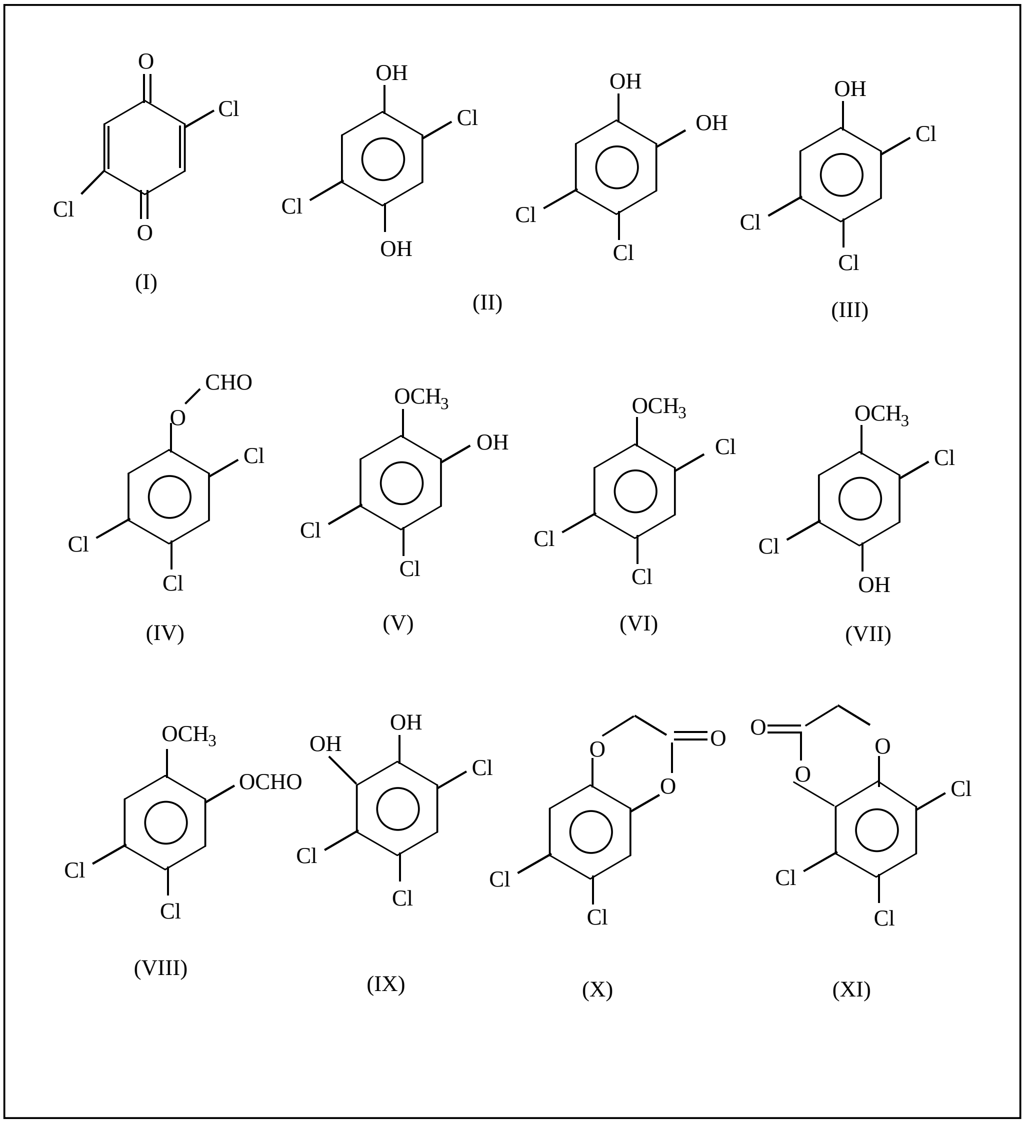
The details of the mechanism are not yet entirely clear (26); however, it seems plausible, by simple analogy with the photodegradation of 4-chlorophenol (27) that repeated hydroxyl attack on the aromatic nng will lead to These observations agree well with t~lOse obtained by Zafirious and coworkers (3) on the photochemical degradation of [2,4,5- T] in the absence of . Ti02. The generally accepted initial events in the irradiation of semiconductor Ti02 dispersions are summarized by reactions (5) to (9) (3).

chloroine atorns and eventually also to some semiquinoid type of radicals.

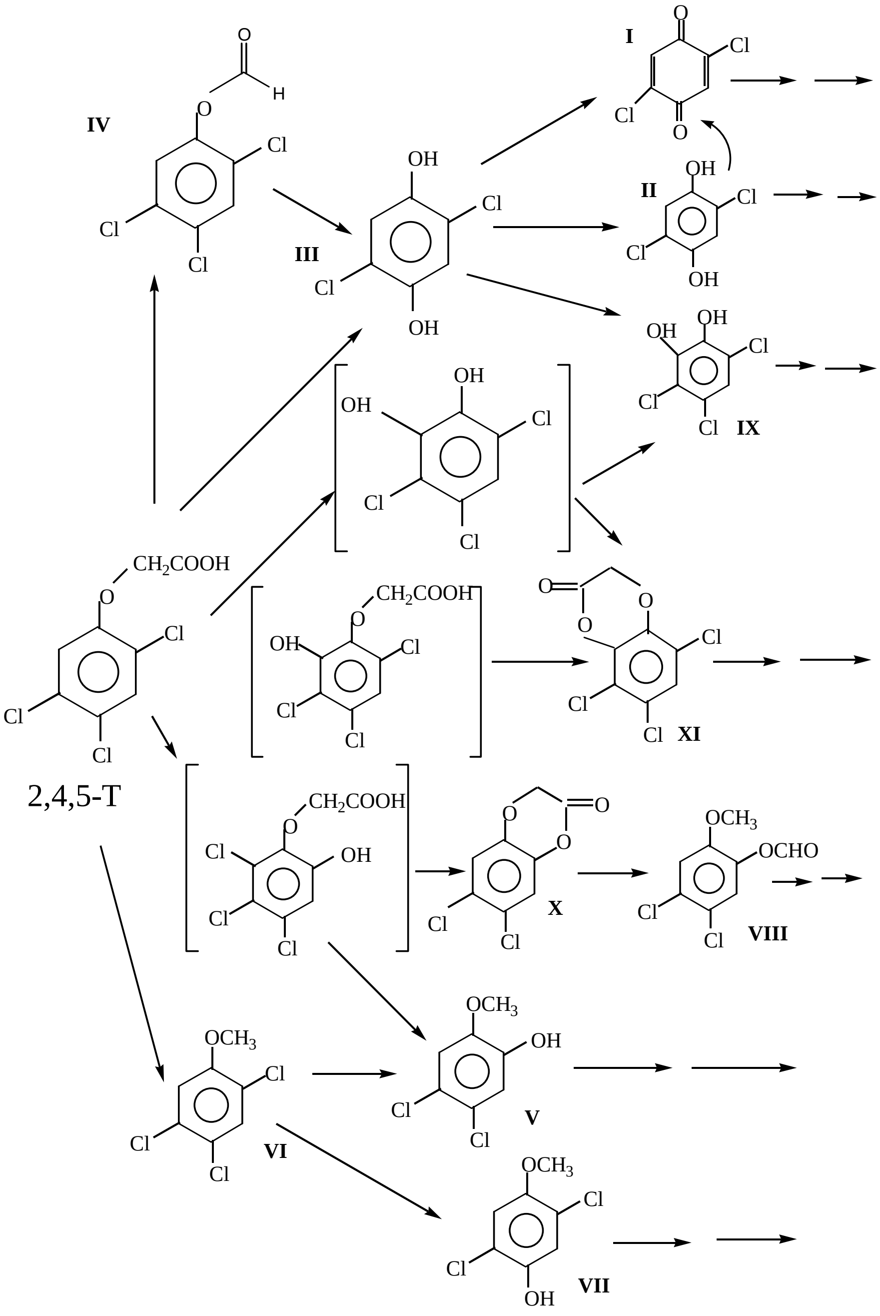
The CI atoms formed undergo subsequent reduction to cr (reaction 10)

$$CI^{0} + e_{ch} \rightarrow CI^{-} \text{...................(10)}$$

The semiquinone radical IS formed can subsequently be oxidized with the resulting benzoquinone undergoing further degradation via photocatalytic oxidation on· $Ti0_2$ as reported earlier (28).



Scheme [1]: The proposed intermediate compounds in the photodegradiation of 2,4,5- trichlorophenol compound.



Scheme [2]: Plausible photodegradation pathway of 2,4,5-T in the presence of TiO_2 under simulated sunlight irradiation conditions

Conclusions

The rate of photooxidation is affected by many parameters such as: solution pH, initial substrate concentration, temperature and $Ti0_2$ loading.

The presence of oxygen (air) is important to initiate the photooxidative degradation process of these compounds.

The results obtained show that both hydroxyl and superoxideradicals are responsible for the initial photooxidative degradation and the aromatic ring cleavage. Addition of hydrogen peroxide increase the rate of photdegradation in all chlorophenols samples.

The activation energy of photocatalytic system investigated in this work proved to be low, and this suggests that these photocatalytic processes are very low sensitive to temperature variations.

It 1S known that the mechanism of photooxidation degradation of hallophenols and other aromatic organic pollutant is different from the thermal oxidation process and the latter usually produces other organic .. compounds which might be more toxic than original substrate. However experiments show that most, if not all, the chlorophenols(19) substrates are converted to inorganic ions and mineral acids (Hel) when irradiated with uv light in presence of $Ti0_2$ semiconductor. This might be of a great advantage from the pollution treatment point of view ovet that of thermal degradation since the final photooxidation production of organic pollutants is non toxic (carbonate, chloride ions and the mineral acids etc).

The present photocatalytic system also works in presence of sunlight though the reaction is slower. The photocatalytic system using sunlight is also affected by solution pH $Ti0_2$ loading, presence of riboflavin sensitized (anatase) and initial chlorophenols concentration.

References

1- O. Hutzinger, The **Handbook of environmental chemistry**, Springer- verlag-Badin 1982.

2- D. Lai, ***J. Environ. Sci. Heath***,C2, 1984, **135**.

3- O. ZafiroLL, J. Joussot Dubien, R. Zeppe and R. Zika, ***Environ. Sci. Technol*, 1984, 18**, 358A.

4- A. Nostrom, K. Anderson and C. Rappe, ***Chemosphere***, 1976**, l**, 21.

5- M. Barbeni, M. Morello, E. Paramauro, E. Pelizzetti, M. Vincenti, E. Borgarello and N. Serpone, ***Chemosphere***, 1987, **16 (6)**, 1165.

6- F. H. Hussein and H. A. Habbeb, ***J. AI-Qadisia***, 2000, **1**, 3.

7- L. Rideh, A. Whehrei', D. Ronze and A. Zoulation, ***Ind. Rng. Chem. Res.* ,** 1997**, 36**, 4712 .

8- T. Koster, J. Slaagger and C. Vander, ***Veen in reference***, 1993**, 134** .

9- J. Chen and C. H. Ni, ***International Regional conference of IOA***, poitiens, France, 1.998, **4,** 1.

10- H. AI-Ekabi and N. Serpone, ***J. Phys. Chem.*,** 1988**, 92** , 5726

11- G. Al-Sayyed. J. Christophe , D'Oliveiro and P. Pichat, ***J. photochelm. photobiol A: chem.*,** 1991**, 58**, 99.

12- Y. Chan, J. Chen and M. Lu, ***Chemosphere***, 2001**, 45,** 29.

13- J. Chen, D. Ollis, W. Rulkens and H. Bruning, ***water : Rcs.*,** 1999**, 33**, 661.

14- A. Mills, R. Davies and Davies and D. Worsley, ***Chem. Soc***., 1993, Rev. 22, 415.

15- A. NEIls, S. Morris and R. Davies, ***J. Photochem., photobiol A70***, 1993, 183.

16- U. Stafford, K. Gray and P. Kamat, ***J. Photochem., Photobiol, 98***, 1994, 6343.

17- Y. Ku; R. Leu and K. Lee, ***Water.· Res., 30(11),*** 1996, 2569.

18- D. Schmelling, K. Gray and P. Kamat, ***Water Res.*,** 1997**, 31**, 1439

19- N. Serpone, ***Solar energy materials and solar cells***, 1995**, 38** , 369.

20- E. Pelizzetti, C. Minero, E. Borgarello and N. Serpone ***Lallgmiurc***, 1993**, 9(11)**, 2995.

21- C. Komann, D. Bahnemann and M. Hoffman, ***Environ. S.ci. Technol***, 1991**, 25**, 494.

22- R. Doong, C. Chen, R. Maithreepala and S. Chang, ***Water Res*.,** 2001**, 35 (12)** ,2873.

23- W. Tang and C Huong, ***Wastemange*,** 1995**, 15 (8)** , 615.

24- S. Aliwi and S. Abdul Kadir, **Ph. D. Thcsis,** University of AL- Mustansiriya (1998).

25- P. W. Atkins **The clements of physical chemistry** ,3rd Edition, Oxford university press, 2000.

27- J. Plimmer, U. Kuliengebiel D. Crosby, and A. Wong, ***Adv. Chem. Ser*.,** 1973**, 120**, 44.

28- M. Barbeni, E. Pramauro, E. Pelizzetti, E. Borgarello, M. Gratzel and N. Serpone, ***Nouv. J. Chim*.,** 1984**,8,** 547.