

## Kinetic Study for 4-chlorophenol Photodegradation in the presence of TiO<sub>2</sub>

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### Abstract

The effects of non-porous powder samples of TiO<sub>2</sub> with specific surface areas about 55 m<sup>2</sup>g<sup>-1</sup> on the kinetics of disappearance of 4-chlorophenol (4-CP) in water, under illumination at  $\lambda \geq 340$  nm (to avoid the direct photolysis of 4-CP) and 298 K, were determined.

The photocatalytic character of the 4-CP disappearance in its presence was shown by (i) the effects of the catalyst mass on the initial rate  $r_0$ , (ii) the Langmuirian -type relationship between  $r_0$  and  $C_0$  (iii) the very low activation energy of 4-CP disappearance (iv) the effect of pH of the medium, (v) the effect of initial concentration  $C_0$  of 4-CP on the rate of photodegradation  $r_0$ . Hydroquinone HQ is the main intermediate in the degradation and none of the toxic biphenyl derivatives produced by direct photolysis was found in presence of TiO<sub>2</sub>. Complete mineralization of 4-CP was eventually obtained, the degradation produced more numerous and more stable aromatic intermediates, as shown by high performance liquid chromatography HPLC tests.

(3)  $C_0$   $r_0$  (2)  $r_0$  (4) TiO<sub>2</sub> (1)  
-4 (5) pH (4) -4  
HQ  
.TiO<sub>2</sub> -4  
4-CP  
. HPLC

### Introduction

Resulting from more severe regulation concerning wastewater, improvements in the existing methods of water treatment, as well as research

into new methods are required. In particular, some new techniques have been proposed that utilize UV light in combination with chemical oxidants producing  $\dot{O}H$  radicals [1-3]. The

coupling of  $\text{H}_2\text{O}_2$  with UV illumination has two disadvantages: the molar absorption coefficient  $\epsilon$  of  $\text{H}_2\text{O}_2$  (Capacity =  $2 \text{ m}^2 \text{ mol}^{-1}$  at 254 nm) [1] is weak and a high concentration of  $\text{H}_2\text{O}_2$  is inappropriate for drinking water. By contrast,  $\epsilon$  of ozone is much higher (Capacity =  $330 \text{ m}^2 \text{ mol}^{-1}$  at 254 nm) [1]; however, the cost of ozone production is one of the limitations of the process [4]. The combination of oxygen (air), UV light and a semiconductor has proved successful in the destruction of model molecules and several classes of organic pollutants in liquid water [5, 6].

Chlorinated organics are abundant pollutants and some of them withstand biodegradation. Among them, monochlorophenols are moderately toxic to aquatic life, but they induce disagreeable taste and odor in water and accordingly impair the flavour of fish even at parts per billion (ppb) ( $\mu\text{g.L}^{-1}$ ) levels [7]. The elimination of these highly soluble pollutant is therefore a necessity. Our study dealing with 4-Chlorophenol (4-CP) completes that regarding the photodegradation of the other two monochlorophenols in aqueous  $\text{TiO}_2$  suspensions [8] and expands preliminary reports [9, 10]. Following earlier work [11] which essentially demonstrated the complete mineralization of 4-CP in the presence of  $\text{TiO}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}$  and UV. Light.

Other reports concerning the  $\text{TiO}_2$ - Photocatalysed degradation of 4-CP have dealt with the effect of pH [12, 13], the fitting of the kinetics of 4-CP disappearance [14] or  $\text{CO}_2$  formation [12, 15] with the Langmuir- Hinshelwood model, the changes in this kinetics in the presence of other chlorophenols [8, 13] and the usage of immobilized  $\text{TiO}_2$  and various photoreactors [12-15]. Hydroquinone was the major

intermediate product detected [13]. In the case of the photodegradation of 3-chlorophenol [16] or the different isomers of monochlorophenol [17] over a  $\text{ZnO}$  powder sample, several intermediates were identified and their kinetics of formation and disappearance were determined [16, 17], as well as the inhibiting effect of ethanol [17].

In this work, the semiconductor mediated photodegradation of 4-CP has been performed under conditions that preclude the direct photolysis of this pollutant, so that both degradation processes could be compared. The effects of various parameters on the initial rate of 4-CP disappearance have been assessed both in respect of basic knowledge of the photocatalytic degradation and potential implementation at finally we have attempted to identify the intermediate products.

## Experimental

### Materials:

Degussa P-25 grade  $\text{TiO}_2$  (mainly anatase, non-porous,  $50 \text{ m}^2 \text{ g}^{-1}$ ). 4-Chlorophenol was obtained from Aldrich (purity greater than 99%) and was employed 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 the photolysis Pyrex cell ( $35 \text{ cm}^3$ ). A magnetic stirrer was used to keep the solution in homogeneous suspension through the photolysis process.

Oxygen gas was passed with rate of  $10 \text{ cm}^3/\text{min}$ . The UV –Visible spectra were recorded with double beam infra- 5 spectrophotometer. The concentration of 4-chlorophenol and

its degradation products were monitored by UV-Visible light spectrophotometer. The incident light intensity was measured by the well known ferrioxalate actinometry<sup>[18]</sup>. The average light intensity between 300-365 nm (medium pressure mercury lamp) is  $9.3 \times 10^{-8}$  Einstein  $L^{-1} s^{-1}$ .

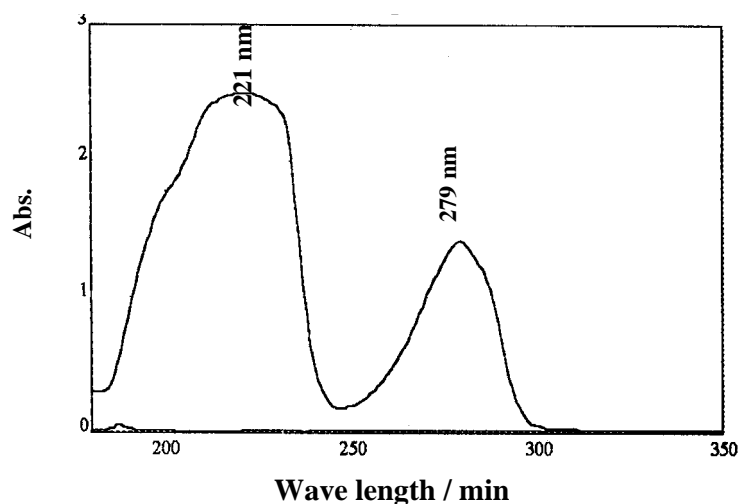
#### **Photodegradation Experiments:**

All photodegradation experiments were carried out by irradiation the aqueous suspension of 4-chlorophenol by UV-Visible light emitted from medium pressure mercury lamp MPML in the 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 was taken, centrifugated and filtrated to remove  $TiO_2$ . In the present work, the photodegradation process for 4-chlorophenol solution in presence of sensitized  $TiO_2$  as photocatalyst were also carried out under sunlight exposure for (8 hrs) during the summer day in 2001.

#### **Result and discussion**

The aqueous solution of 4-chlorophenol ( $10^{-2}$  M) shows two maximum absorption bands at 221 nm and 279 nm as show in figure (1).



**Fig(1): The absorption spectrum of [4-CP] in aqueous medium in the spectral range between 200-350 nm. At pH = 6.4, 298 K, without  $TiO_2$ , Stock solution ( $10^{-2}$  mol.  $L^{-1}$ ).**

The second band at 279 nm was used to monitor the photocatalysis on the degradation of 4-CP to study the optimum condition and the effect of

different parameters on the degradation of 4-CP.

### Effect of solar radiation without TiO<sub>2</sub>

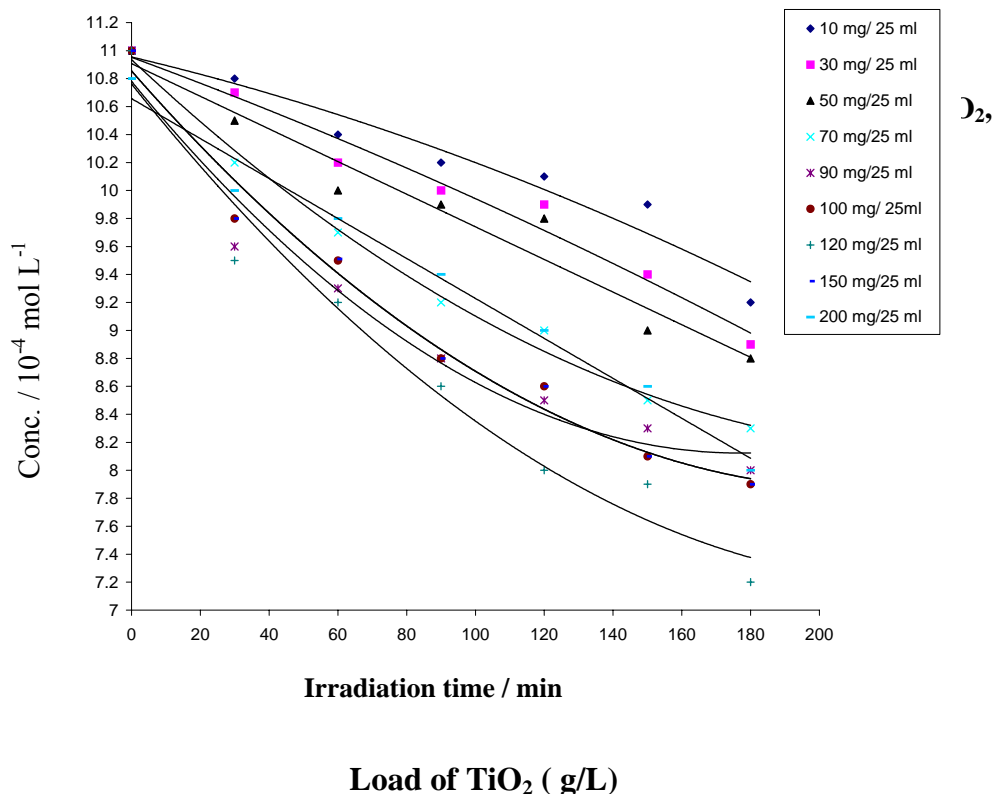
The reaction vessel was exposed to the UV radiation from solar without TiO<sub>2</sub> for 3 hr. It was noticed that 4-CP is quite stable under solar condition this mean that light, O<sub>2</sub> and TiO<sub>2</sub> are very essential for photocatalytic degradation of 4-CP [19].

### Effect of TiO<sub>2</sub>

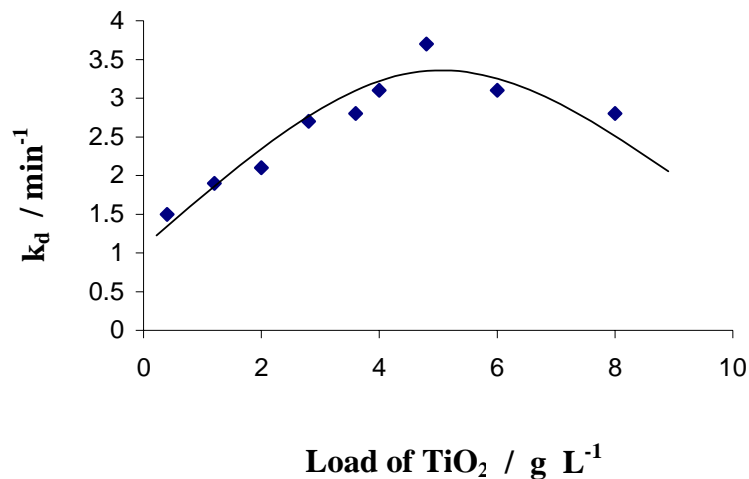
A series of experiments have been done by using different weights of TiO<sub>2</sub> in presence of O<sub>2</sub> and light at 298 K.

Figure (2) shows maximum value of the rate has been obtained at 120 mg of TiO<sub>2</sub> for 25 cm<sup>3</sup> of the solution so that this quantity will be chosen to study the effect of other parameters. The rate of photocatalytic degradation of 4-CP has been increased with amount of catalyst due to complete absorption of incident light potentially absorbable by TiO<sub>2</sub> [19].

Figure (3) shows the rate of photodegradation is increased with increasing of TiO<sub>2</sub> weight and this observation can be explained that a large number of TiO<sub>2</sub> particle from inner filterate [20] which absorbs high portion of incident light as well as scatters parts of it.



**Fig. (2): Relation between  $k_d$  of 4-CP photodegradation and TiO<sub>2</sub> loaded=4.8 g. L<sup>-1</sup>, At 298K, pH = 6.4, initial concentration =  $10^{-3}$  M**



**Fig. (3): Relation between  $k_d$  of 4-CP photodegradation and  $\text{TiO}_2$  loaded=4.8 g L<sup>-1</sup>, At 298K, pH = 6.4, initial concentration = 10<sup>-3</sup> M**

***Effect of temperature and determination the activation energy ( $E_a$ )***

To study the effect of temperature, a series of experiments were carried out over a range of temperatures from 283 to 303 K. These experiments were carried out under illumination with light of  $\lambda = 366$  nm (from OSRAM Lamp). The results are shown in Fig. (4) [4-CP concentration versus irradiation time].

283 K to 303 K. The activation energy of 4-CP disappearance deduced from the plot is [23 kJ. Mol<sup>-1</sup>]; it indicates that thermally activated steps are negligible, *i.e.* adsorption/desorption processes are almost temperature –independent in this domain on the surface of  $\text{TiO}_2$ .

Fig.(5) shows the Arrhenius-type plot in the range of temperatures from

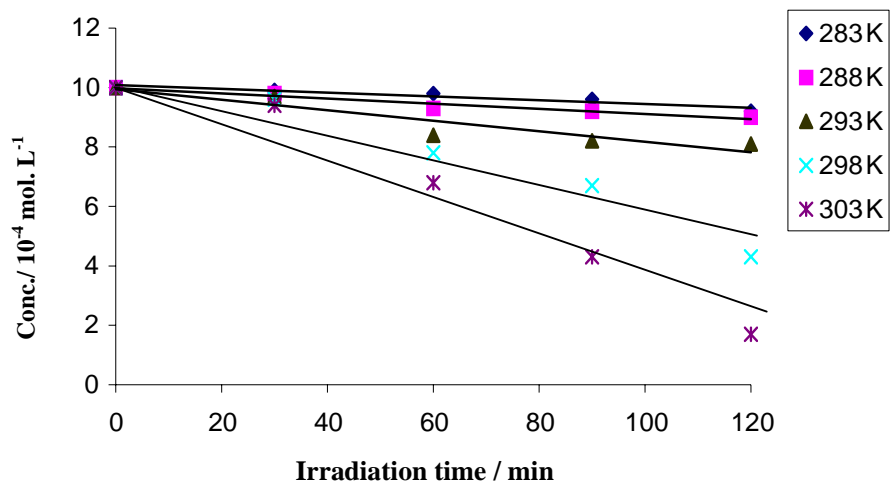


Fig. (4): Effect of temperature on the rate of photodegradation of 4-CP , initial concentration of 4-CP is  $1 \times 10^{-3}$  mol L $^{-1}$ , initial light intensity =  $9.3 \times 10^{-8}$  Einstein L $^{-1}$ s $^{-1}$ , pH = 6.4.

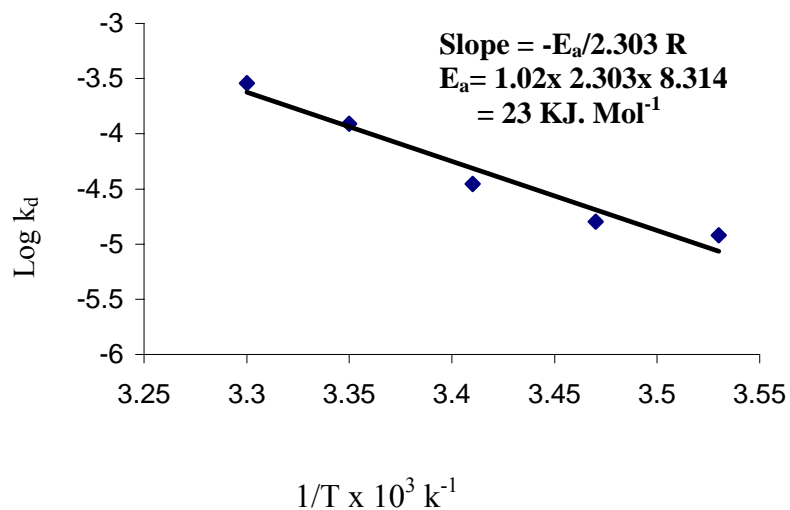


Fig. (5): Shows Arrhenius equation by using naked TiO $_2$  , initial concentration of 4-CP is  $1 \times 10^{-3}$  mol L $^{-1}$ , initial light intensity =  $9.3 \times 10^{-8}$  Einstein L $^{-1}$  s $^{-1}$ , pH = 6.4.

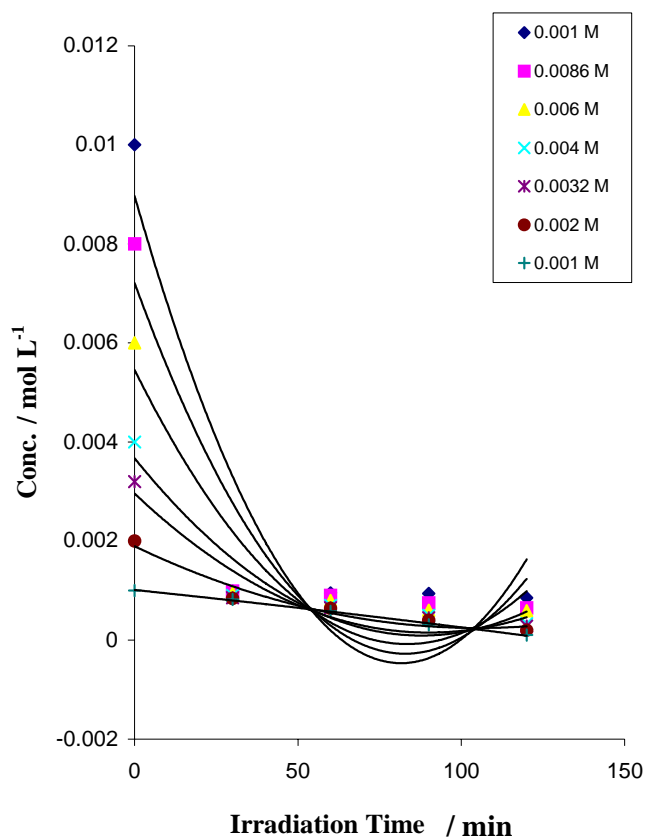
**Effect of initial concentration of 4-chlorophenol [4-CP] on the rate of photodegradation reaction**

A series of experiments have been done by irradiation for

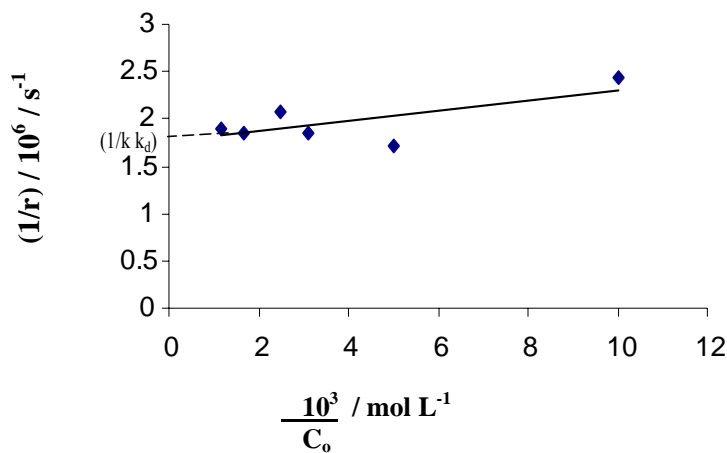
different concentrations of 4-CP by taking different solutions volumes (2.5,5,8,10,15,20,25) ml from  $10^{-2}$  M 4-CP and 0.12 gm  $\text{TiO}_2$  /25 ml. The results are shown in the table (1) and Figs.(6 and 7).

**Table (1): The initial rates of 4-CP disappearance at different initial concentration ( $C_0$ ), with 0.12 g /25 ml  $\text{TiO}_2$  loading and initial pH of 6.4.**

$C_0$ / $\text{mol L}^{-1}$	$k_d$ $/ 10^{-4} \text{ s}^{-1}$	$t_{1/2}$ /min	Observed rate / $10^{-7}$ $\text{Mmol s}^{-1}$	Calculated rate / $10^{-7} \mu\text{mol s}^{-1}$
$1 \times 10^{-3}$	4.12	28.0	4.12	5.69
$4 \times 10^{-3}$	1.21	95.45	4.84	5.83
$6 \times 10^{-3}$	0.90	128.33	5.40	5.84
$8.6 \times 10^{-3}$	0.69	172.38	5.762	5.85



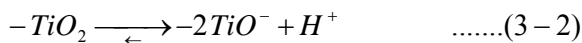
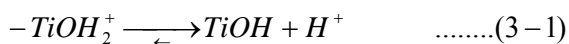
**Fig. (6): Effect of different initial concentrations on the rate of photodegradation of 4-CP. At 298K, pH= 6.4 and 10ml  $\text{m}^{-1}$  flow rate as a function of time.**



**Fig. (7): Plot of the rate Vs the initial concentration of 4-CP photodegradation disappearance in aqueous  $\text{TiO}_2$  ( $4.8 \text{ g L}^{-1}$ ) at 298K.**

#### *Effect of different initial pH*

The pH value at which the surface of an oxide is uncharged is defined as the zero point charge



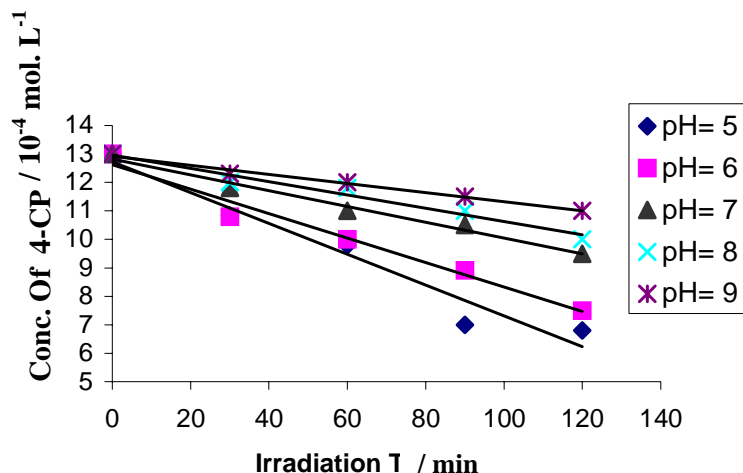
Kormann and coworkers<sup>[24]</sup> has calculated these equilibrium constants which are equal to  $\text{pK}_{\text{TiOH}} = 2.4$  and  $\text{pK}_{\text{TiO}^-} = 8.0$  and evaluated the abundance of all the species as a function of pH:  $-\text{TiOH} \geq 80\%$  when  $3 < \text{pH} < 10$ ,  $\text{TiO}^- \geq 20\%$ , if  $\text{pH} > 10$  and  $-\text{TiOH}_2^+ \geq 20\%$  when  $\text{pH} < 3$  under these conditions, the photocatalytic degradation of the organic ionizing compounds is strongly affected by the pH of the solution

( $\text{pH}_{\text{ZPC}}$ ), which for Degussa P-25  $\text{TiO}_2$  is 6.25 [Kormann and coworkers<sup>[24]</sup>. Above and below this value, the catalyst is positively or negatively charged according to:

[Pelizzeti<sup>[25]</sup> and Pichat<sup>[26]</sup>] studied this effect.

Therefore it was necessary to investigate the effect of solution pH value on the rate of photocatalytic degradation. A series of degradation experiments have been done in the pH range from 5.0 to 9.0 as Fig (8).





**Fig. (8): Relation between the concentration of 4-CP with illumination time (min) at different pH solution.**

#### **HPLC analyses:**

The course of photolysis process of 4-chlorophenol on  $\text{TiO}_2$  surface was also monitored by HPLC (chromatogram) of 4-chlorophenol [4-CP] irradiation. Before irradiation, the HPLC (chromatogram) showed the absorbance peak, which appeared at retention time of 3.87 minutes, while after irradiation the intensity of this peak is gradually decreased with irradiation time.

In literature [24, 25] six primary intermediates were detected by HPLC technique under the indicated conditions. All of which disappeared within nearly the same illuminations time as 4-chlorophenol [4-CP]. Three of these intermediates were identified by HPLC as hydroquinone [HQ] 1,4-benzoquinone [BQ] and 4-chloro 1,2-dihydroxybenzene [CDHB]. The other three intermediates were not identified because of their low concentration in the reaction mixture. The abundance of these intermediates conc. follows the

following trend: HQ >> BQ >> CDHB >> 3 other intermediates.

The maximum concentration of HQ in a typical run was less than  $0.2 \text{ mg. L}^{-1}$  for the initial concentration of  $20 \text{ mg. L}^{-1}$  of 4-CP. Moreover, the HPLC analysis in Fig (9) showed the absorbance of 1,2-dihydroxybenzene [Catechol], 1,3-dihydroxybenzene [resorcinol] as well as biphenyl derivatives. The absence of these latter compounds are very important because of their presumed toxicity.

Independent experiments have shown that HQ was readily degraded under the same experimental conditions in agreement with previous studies of [Al-Sayyed and coworkers]

[10] which explains its maximum BQ was also rapidly degraded. No attempt was made to identify the secondary intermediates enroute to total mineralization, i.e . formation of CO<sub>2</sub> and HCl. However, from the decrease in pH observed during the first 10 min of illumination, it seems reasonable to suggest that the aliphatic organic acids are formed as secondary intermediated as proposed in the case of phenol according to results reported by Okamoto and coworkers<sup>[26]</sup>.

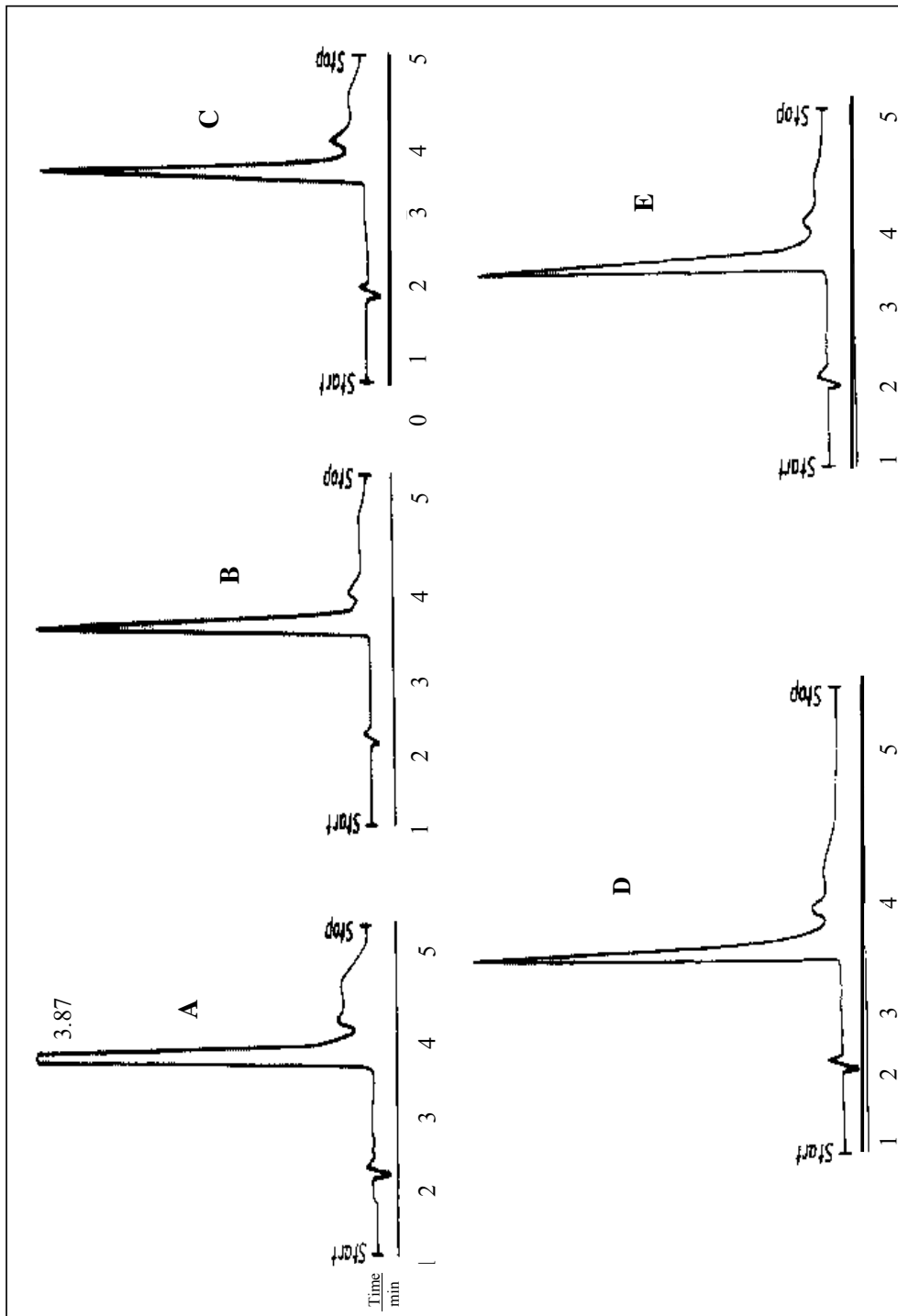
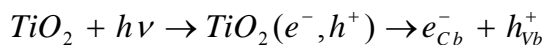


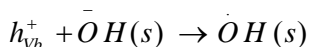
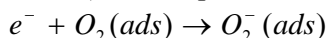
Fig. (9): HPLC chromatogram of 4-chlorophenol [4-CP] Solution [(A) before photolysis (B) after 60 min (C) after 120 min (D) after 180 min (E) after 240 min] irradiation. Initial [4-CP] concentration was  $10^{-4}$  mol. L $^{-1}$ . TiO $_2$  loading was 4.8 gm. L $^{-1}$  and oxygen flow rate 10 ml. min $^{-1}$ . The HPLC operating conditions were : mobile phase methanol: water mixture (65: 35 V/V) Column 25 cm x 4.6 mm C $_{18}$  and uv. Detector.

**Mechanism of Reaction:**

Photocatalytic oxidation of 4-chlorophenol (4-CP) in the presence of  $TiO_2$ , air, and ultraviolet radiation takes place according to the following mechanisms:



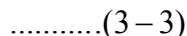
were  $e^-$  electron conductance band Photoelectrons are trapped by adsorbing oxygen ( $O_2$  ads), while photoholes are trapped



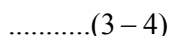
These radicals are reacted with adsorbed molecules of 4-chlorophenol and abstract hydrogen atom which produces the

**Naked  $TiO_2$** 

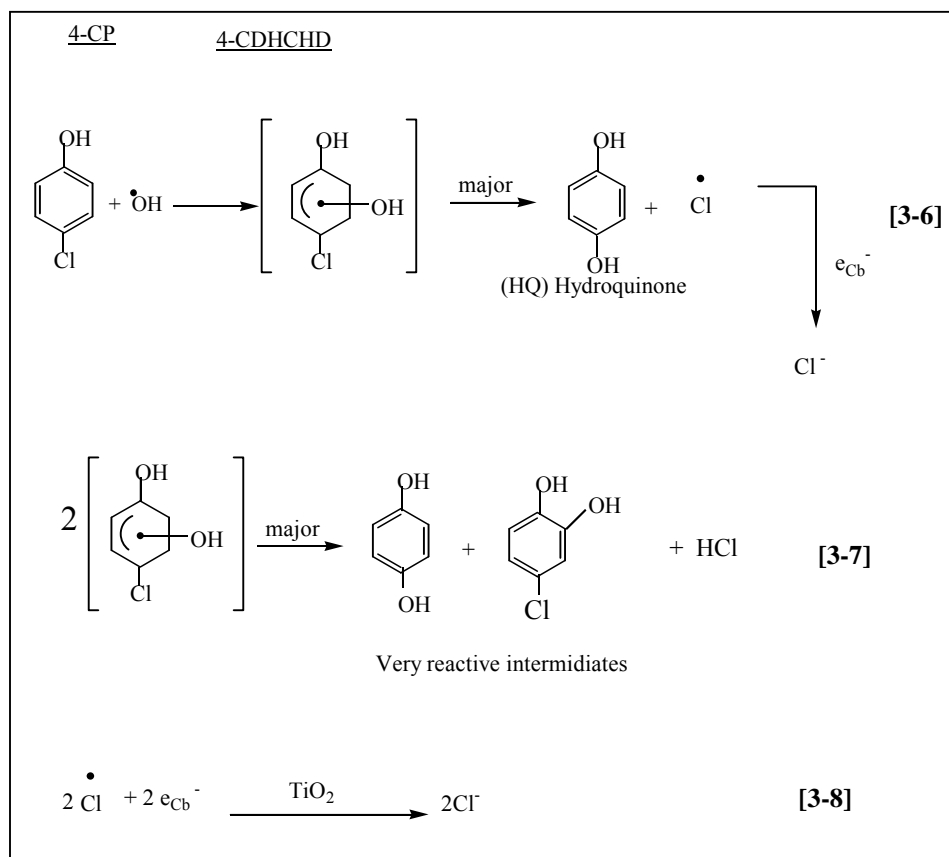
In this mechanism, the first step is the excitation of semiconductor particles to generate conduction band electrons and valence band holes, and their separation.



by the surface hydroxyl groups as in the following equations.



corresponding intermediates products [27-29] as in the following equations:

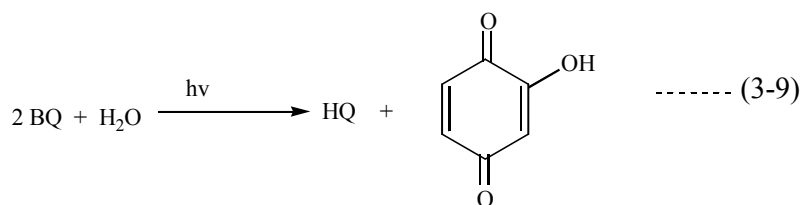


Reports in literature indicate that, in the absence of  $TiO_2$  the rate of cleavage of C-Cl of aromatic ring is very slow. In contrast, and in the presence of  $TiO_2$ , the photooxidative degradation occurred by the electrophilic reaction of OH radical on the benzene ring which is produced the highly reactive intermediates responsible to ring-opening products.

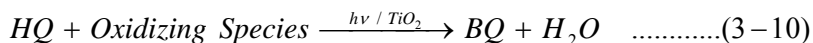
In the present study, the OH radicals generated on  $TiO_2$  surface either abstract hydrogen or attack aromatic ring and chlorine atom.

To determine the interrelated reactions between 4-CP, HQ and BQ, a solution containing a few ppm of each of these compounds was illuminated at  $\lambda \geq 340\text{nm}$  in the presence and

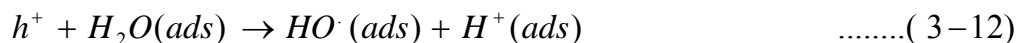
absence  $TiO_2$ . In the absence of semiconductor, the concentration of BQ decreased rapidly while that of HQ increased and then levelled off, and that of 4-CP did not vary as expected, in the presence of semiconductor; the amount of BQ first decreased rapidly and then more slowly (as expected because of the photocatalytic formation of Q from 4-CP via HQ), while that of HQ first increased markedly (as expected if HQ is formed from both BQ and 4-CP) and then decreased; all the compounds disappeared within about the same illumination time. In short, these experiments show the coexistence of the following photochemical (equation (3-6)) and photocatalytic (equation (3-7)) reactions at  $\lambda \geq 340\text{nm}$ .



And



Finally, the radicals formed during this mechanism are responsible for the oxidation of (CPs) yielding some intermediate compounds and mineralization products [30].





## Conclusion:

The rate of photooxidation is affected by many parameters such as: solution pH, initial substrate concentration, temperature and TiO<sub>2</sub> 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 superoxide ( $O_2^{\cdot-}$ ) radical are responsible for the initial photooxidative degradation and the aromatic ring cleavage. Addition of hydrogen peroxide increase the rate of photodegradation in all chlorophenols samples.

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

It is known that the mechanism of photooxidation degradation of chlorophenols and other aromatic organic pollutant are 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 substrates are converted to inorganic chloride ions and acid (HCl) when irradiated with uv light

in presence of TiO<sub>2</sub> semiconductor. This might be of a great advantage from the pollution treatment point of view over that of thermal degradation since the final photooxidation production of organic pollutants is non toxic (carbonate, chloride ions and the mineral acid .....etc).

The present photocatalytic system also can carried on by sunlight though the reaction is slower. The photocatalytic system using sunlight is also affected by solution pH, TiO<sub>2</sub> loading, presence of riboflavin sensitized (anatase) and initial chlorophenols concentration.

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