Quantitative Study of Photocatalyst Degradation of Propanil Herbicide in Water Using different Analytical Methods

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ABSRTACT

In this study the photocatalytical degradation of propanil that used frequently in Iraq was investigated in different sources of water (distilled, tap and river waters) by using zinc oxide as a photocatalyst and mercury lamp as a source of light with intensity 2.66 x 10^{-4} Ein.l^{-1} sec.$^{-1}$. The rate of photo oxidation process is followed-up under optimum conditions at natural pH of solution, 10^{-4} M initial concentration of propanil, 0.4 g/lZnO loading and 20 ml/min oxygen flow rate. The photodegradation rate measurements were based on chloride ions liberation and the change in conductivity and pH. Kinetic study of photodegradation was found that the reaction is of the first order reaction and found equal to 0.0046, 0.0079 and 0.0086 min^{-1} for distilled, tap and river waters, respectively. Also the activation energy and quantum yields were calculated. UV-Visible spectrophotometric and PHLC were utilized to identify final species of the reaction products.

Keywords: Propanil herbicide, Photocatlytical degradation, Different analytical methods

INTRODUCTION

Pesticides are grouped with large collection of toxic chemicals that can affect human health when found at certain specific concentration above maximum contaminate level in drinking water and the contamination of ground water with pesticides is a subject of international importance [1] .Propanil is an anilide and postemergence herbicide,$C_9H_9Cl_2NO$, used for weed control on potatoes, rice and other crop plants [2.] Propanil absorbed into the body through ingestion, inhalation or dermal exposure, it cause central nervous system depression. The probable oral lethal dose (LD50) is 0.5 – 5.0 g/kg of body weight [3]. One of the most common pesticide degradation reactions is the photodegradation which breakdown of pesticides by light particularly sun light; there are several parameters which are effect the rate of degradation discussed by Topalovet al.[4]. The photocatalytic oxidation of organic compounds including pesticides in water is the subject of a large body of researchers [5]. Semiconductors has arisen out of the development of growth technologies for the fabrication of high quality single crystals and epilaxial layers, allowing for the realization of ZnO-based electronic and photoelectronic devices, with a wide band gab of 3.2 eV and large binding energy of 6 mV at room temperature [6] . Habibi et al.[7]studied photodegradation of several aniline derivatives using aqueous solutions containing ZnO in the range 6.46 x 10^{-3} min^{-1} to 2.59 x 10^{-2} min^{-1} . Several papers were published for measuring some pesticides by HPLC, Abdul-Kadir[8]was measured the degradation rate of the pesticides, propanil, carbaryl and behomyl by using HPLC method. Davis et al.[9] used HPLC with reversed phase column and UV detection for degradation of organophosphate pesticides, dicrotophos and dichlorovos in natural and distilled waters. Sadiket al.[10] studied Thephotodecolorization of neutral red dye. It has been carried out using a combination between ZnO and UV radiation (λ=254nm) at a pH of 6.It was observed that the dye decolorization was enhanced using UV/ZnO. First-order kinetics adequately described the disappearance of the dye. Ameta et al[11]used ZnO to study the photoelectrocatalytic degradation of picric acid which was experimentally investigated using a two electrode system. The decomposition of substrate was observed to be affected by photo catalytic characteristics. Kinetics of reaction was found to be affected by parameters like concentration of substrate, pH, amount of semiconductor, light intensity, cell voltage, radical quencher and band gap, etc. Probable mechanism for the photoelectro catalytic degradation of picric acid is proposed. The effect of ZnO loading has been studied by number of researchers, Parida and Parija[12]has shown the best ZnO loading on photocatalytic degradation of phenol was 0.8 g/l. Evgenidou et al. [13]studied the increase of temperature from 30 to 35 ºC on the photocatalytic degradation of dichlorovos using TiO_2 and ZnO as catalysts. They found that the enhancement of the photo oxidation with increase of temperature due to increasing collision frequency of molecules. In this work the photocatalytic degradation of propanil herbicide using zinc oxide as a catalyst. The photodegradation products were controlled by measuring chloride, carbonate and nitrate ions and the change in conductivity and pH. The rate of degradation, the kinetic and quantum yield were measured and also UV-Visible spectrophotometric and HPLC were used.

2. Experimental

1. Photolytic cylindrical pyrex cell volume 75 ml fitted with water jacked for temperature control. The cell window was made from quartz and the cell supplied with two opens of 0.5 cm in diameter used for gas purging and sampling processes.
2. The ultraviolet light source was mercury lamp, 1Ampir, OSRAM from Germany, the light intensity 2.66 x 10^{-4} Ein.L^{-1} S^{-1}.

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3. Chloride ion selective electrode type Orion model 94-17.
4. Conductivity meter type WTW LF 191, Germany.
5. pH meter type Philips PW 9420.
6. Centrifuge type (REMI R&C Laboratory centrifuge), England.
7. UV-Visible spectrophotometer type Shimadzu 1650, Japan.
8. HPLC type Knaner, Germany.
9. Dist TDS meter range 10 – 1990 type Hanna, Italy.
10. Analytical balance type (sartorius BL 210 S)
11. Multiparameter bench photometer (C99HANNA, Hungary)
12. Gas Chromatography (GC, Packard 438 A, USA)

2.1 *Chemicals and reagents*

Propanil supplied from Iraqi See Company as aemulsifiable concentration (Stam F-34,360 g/l active ingredient with purity of 35%.Zinc oxide supplied from BDH company purity of 99%, the band gab of 3.4 eV at $0°K^{14}$ with maximum absorption spectrum at 370 nm[15].Oxygen gas with purity 99.99% was used. Standard solution of 10^{-4} Molar (21.8 ppm) propanil was prepared in different waters (tap, river and distilled).Stock solution of KCl was prepared by dissolving 1.8625 g in 250 ml water and by serial dilution, 10^{-2} to 10^{-6} M were prepared for calibration of chloride electrode.

2.2 *Water Samples*

Different water samples have been used in these investigation (distilled, tap, and river water) .Their physicochemical characteristics is given in Table-1.

Table-1: Physicochemical Characteristics of Selected Water.

Water type	Distilled Water	Tap Water	River water
PH	6.9	8.3	8.3
Conductivity µs/cm	2	749	755
TDS(mg/l)	0	180	190
DOM**(mg/l)	nd*	nd	2
Salinity %	nd	0.449	0.456
Cl⁻(mg/l)	nd	549.8	524.8
NO_3^-(mg/l)	nd	0.27	1.43
$CO_3^=$(mg/l)	nd	120	123
$SO_4^=$(mg/l)	nd	87.8	168.7

nd* not determined
**dissolved organic matter/ determination by GC

The natural water samples were obtained from Baghdad Al-Zaafarania city, Iraqi location. The collected water samples were stored in a poly ethylene bottles which cleaned with distilled water and 0.1M nitric acid and dried. All water samples were kept in refrigerated at 4 C° prior to use.

2.3 *Procedures*

The photolysis experiments were carried out in a photolytic cylindrical Pyrex cell (volume 75ml) which is diagrammatically fitted with water jacket for temperature control. The cell is supplied with two openings of (0.5cm) in diameter and these were used for gas purging and sampling processes.

Zinc Oxide powder was added to an aqueous solution of known concentration of propanil solution mixture, and then the solution was saturated with oxygen with a continuous flow prior the photolysis process. Magnetically stirred reaction mixture in photo reactor was irradiated with mercury lamp. Five milliliter samples were taken at various irradiation time intervals, The Zinc oxide was removed from the samples by using centrifuge .Photo degradation product were identified by different analytical technique and by comparing retention time with authentic samples by using chromatographic HPLC and UV. Visible spectrophotometer techniques. To minimize the possible dark reactions, all samples were kept in the refrigerator in the dark. The effect of temperature on photolytic reaction was monitored by adjusting the temperature of the circulating water between 25-45C°.The contents of reaction flask were continuously stirred by magnetic stirrer.

2.4 *Calculations*

The rate constant of the decomposition of pesticides (K_d) was determined by equation 1[16].

$$Ln\ (\ A_t - A_{\alpha\ )} = Ln\ (\ A_o - A_\alpha\ ) - K_d t(1)$$

Where A_t: the absorbance at time irradiation.
A_∞: the absorbance for infinite time of irradiation
$A_\circ$: the absorbance before irradiation
k_d: specific the rate constant
t: time of irradiation.

A titration method [17].was used to determine total carbonate ions in various sources of waters at the infinite times of photodegradation.

Quantum yield (Φ) in photocatalysis may be defined as a number of moles of products formed or destroyed per mole of photons introduced in the system[18]

$$\Phi = rate\ of\ reaction\ /\ photon\ flux\ (2)$$

In the present work, the quantum yield was determined for propanil degradation in distilled water after determined the intensity of light ($I_\circ$)[19,20] and determined the intensity of absorbent light according the following equations:

$$I_{abs.} = I_\circ\ (1 - e^{-\ (\varepsilon.c.b)})\qquad (3)$$
$$\Phi = rate/I_{abs} = k\ [c]\ /\ I_{abs}(4)$$

3. RESULTS AND DISCUSSION

The photocatalytic degradation of propanil in different sources of water was studied by following up the concentration of the chloride ions released, conductivity and pH change during the irradiation time. The optimum conditions were measured for degradation of propanil including, initial concentration of propanil, quantity of zinc oxide loading, flow rate of oxygen gas and time of irradiation using distilled water. The effect of changing concentration of propanil in the range $10^{-1} - 10^{-6}$ M was studied for photodegradation, after 5 hours of irradiation in distilled water the results of chloride ions released ware measured by chloride selective electrode, conductivity and pH values are listed in Table 2. The maximum concentration of chloride ion, 1.836μg/ml was noticed at 10^{-4} M of propanil, conductivity at 93 μs/cm and pH was 6.8. Therefore, the concentration of propnanil at 10^{-4} M was fixed in this work. The influence of photocatalyst load on the photodegradation of propanil has been investigated by employing different quantities of zinc oxide ranged from 0.13 to 0.8 g/l at fixed concentration of propanil, 10^{-4} M in distilled water, the results are listed in Table-2.

The optimum loading of zinc oxide gave maximum chloride concentration of 5.031 μg/ml and conductivity of 181μs/cm at 0.4 g/l of zinc oxide. Above this loading, the decomposition percentage gradually decreases and this might be explained by the fact that ZnO suspension become more opaque to the incident light and therefore, the light absorption will be limited only to the first layer of the photocatalytic mixture and the rest of the solution can not be receive the light.

Moreover, light scattering at high ZnO loading becomes more effective and decrease the photo intensity. These results are in a good agreement with several researchers when they using semiconductor for photocatalysis of the polluted molecules [21,22].

Other important parameter studied was the effect of oxygen flow rate on the photodegradation of propanil in distilled water. Table 1 shows the values of oxygen flow rate varying from 10 to 50 ml/min in zinc oxide loading of 0.4 g/l and initial concentration of propanil 10^{-4} M. A maximum percentage of degradation of propanil at 90.12% was

Table 2: The values of chloride concentration, conductivity and pH change after 5 hours of irradiation at optimum conditions of degradation.

Study of propanil Concentration				Study of ZnO loading				Study of O$_2$ flow rate			
Conc. of propanil (M)	Cond. μs/cm	Cl^{-1} ion ppm	pH change	ZnO loading	Cond. μs/cm	Cl^{-1} ion Ppm	pH change	O$_2$ flow rate ml/min	Cond. μs/cm	Cl^{-1} ion ppm	pH change
10^{-1}	45	0.105	7.9	0.13	157	0.920	7.3	10	180	8.100	6.0
10^{-2}	53	0.213	7.8	0.26	170	2.805	6.5	20	202	6.390	5.8
10^{-3}	70	0.765	7.6	0.40	181	5.031	6.0	30	177	5.500	6.5
10^{-4}	93	1.836	6.8	0.53	167	1.840	6.7	40	165	4.030	6.9
10^{-5}	81	1.065	7.6	0.60	161	1.310	7.1	50	163	3.150	7.3
10^{-6}	58	0.390	7.5	0.80	153	0.780	7.8				

obtained at 20 ml/min flow rate of oxygen, at this flow rate a higher values of chloride ions and conductivity were noticed and lower values of pH was obtained. As the flow rate of oxygen increase the photodegradation was also increase due to the more adsorption on the surface of the catalyst (ZnO) by the species obtained from the photodegradation. Above 20 ml/min flow rate the photodegradation start to decrease because many of molecules substrate accumulated on the adsorption sites and this cause a decrease in the adsorption on the surface of the catalyst. The effect of light on the degradation of propanil in different sources of waters (distilled, tap and river) under the fixed conditions , concentration of propanil at 10^{-4} M, loading of ZnO at 0.4 g/l and flow rate of oxygen at 20 ml/min was studied and the results of measuring chloride concentration, conductivity and pH change after degradation are listed in Table-3.

Table-3: Values of chloride ion, conductivity and pH after irradiation times of propanil of 10^{-4} M and ZnO loading of 0.4 g/l.

Irradiation time /min	River water			Tap water			Distilled water		
	Chloride ppm	Cond, μs/cm	pH change	Chloride ppm	Cond. μs/cm	pH change	Chloride ppm	Cond. μs/cm	pH change
0	0	768	8.5	0	748	8.4	0	7.0	8.5
30	0.79	793	7.9	0.32	755	8.0	0.41	18	8.1
60	1.58	818	7.8	1.12	773	7.8	0.98	37	7.8
90	2.21	847	7.6	1.72	795	7.7	1.68	55	7.7
120	2.96	861	7.3	2.41	811	7.4	2.29	74	7.5
150	3.43	890	7.1	3.07	827	7.2	2.96	95	7.3
180	4.26	928	6.8	3.77	845	6.9	5.53	115	7.0
210	4.91	955	6.5	4.45	863	6.6	4.18	134	6.8
240	5.56	1005	6.1	5.11	882	6.3	4.85	154	6.5
270	6.17	1038	5.9	5.85	899	6.0	5.45	173	6.1
300	6.78	1088	5.5	6.4	921	5.7	6.39	202	5.8

The results in Table-3 were compared with the results without exposure the propanil to the light. The chloride concentrations in the dark (no light) was 0.01 ppm during 300 min of irradiation, as well as no change or very small change in conductivity from 750 to 920 μs/cm for both river and tap waters and from 7 to 30 μs/cm for distilled water. A typical plot shows the increase of chloride ion concentration with irradiation time under fixed conditions of the degradation of propanil in distilled water, tap water and river water is shown in Fig-1.

The increasing of chloride ion concentration. in aqueous medium river water could be the best medium for the photodegradation process because of the mineral salts it includes. These kinds of salts cause an increase in the rate of photodegradation The rate of photodegradation of propanil was measured by plotting Ln ($A_t - A_o$) versus irradiation time, the decrease in concentrations of propanil was monitored by following the absorption at λ_{max} 248, 247.6 and 246.4 nm in distilled, tap and river waters, respectively. A straight line was obtained which can be suggested the reaction is the first order kinetic of the photolysis process.

From the slopes of the straight lines, the specific rate constant K_{photo} in the waters and the half-life of the reactions were evaluated and listed in Table 4.

Series of experiments were carried out at different temperatures ranged from 298 K to 318 K in order to investigate the effect of temperature on the photocatalytic degradation rate of propanil in aqueous zinc oxide suspension. It has been found that the rate of propanil photodegradation is directly proportional with increasing temperature. The enhancement of the photo oxidation with the increase of temperatures is probably due to the increasing collision frequency of molecules. Irradiation is believed to be the primary source of e^- h^- pairs at ambient temperature because the band gap is too high to overcome by thermal excitation [23,24].

Table-4: Kinetic parameters of photocatalyst of propanil in water at different temperatures

Temp.	River water				Tap water				Distilled water			
	K_{photo} (min^{-1})	$T_{1/2}$ (min)	R^2	%RSD*	K_{photo} (min^{-1})	$T_{1/2}$ (min)	R^2	%RSD	K_{photo} (min^{-1})	$T_{1/2}$ (min)	R^2	%RSD
298 K	0.0086	80.6	0.9994	6.16	0.0079	87.72	0.9992	6.33	0.0046	150.6	0.9992	6.52
308 K	0.0135	51.3	0.9996	Nd	0.0116	59.7	0.9994	nd	0.0055	126.0	0.9995	nd
318 K	0.0179	34.8	0.9990	Nd	0.0172	40.3	0.9991	nd	0.0063	110.0	0.9991	nd
E_a	28.7 KJ/Mole				30.8 KJ/Mole				22.8 KJ/Mole			

* Average of five determinations

(nd) not determined

The results in Table-4 demonstrate that the photolysis degradation of propanil was greater in both river and tap waters compared to the distilled water.the degradation of propanil in river water gave a good result than the degradation in tap and distilled water in analyzing the tablets have RSD% about 6.16 for degradation of propanil in river water, that

means have a good precision than degradation in tap and distilled water in which RSD% equal 6.33 and 6.52 respectively.
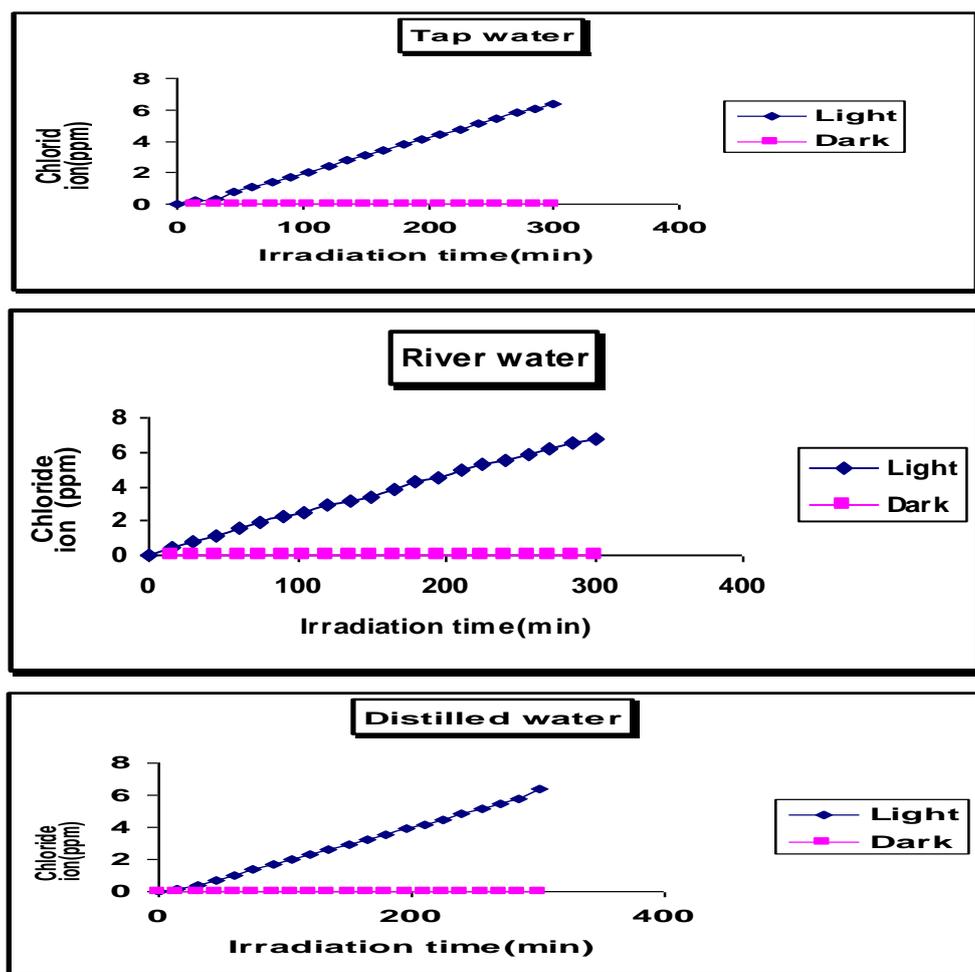

Fig-1: Relation between chloride concentrations with irradiation time ofpropanil in waters.

The high degradation of propanil in river water is due to the constitution of the irradiation media that significantly enhanced the degradation. For example, the presence of 2 ppm dissolved organic materials in river water can cause an increase the degradation. The second reason is the presence of nitrate ions in river water and tap water with concentrations 1.43 and 0.27 ppm, respectively, which enhanced the degradation process. Also the nitrate and nitrite ions in water can absorbed light at wavelengths 355 and 303nm which can produce free radicals (OH·) during the photolysis which accelerate the organic reactions leading to the degradation of propanil.

Also the sulfate and carbonate ions in river water can effect the photodegradation. The sulfate ions in tap and river are 87.8 and 168.7 ppm and carbonate around 120 ppm which effects the degradation. The third reason for enhancing the degradation rate of propanil in river and tap waters is the presence of cations, such as calcium concentrations are 28.3ppm and 20 ppm and magnesium concentration are 6.9 and 6.7 ppm, in river and tap waters respectively,which take part in complexation reactions and enhancing the photolysis of organic compounds, these results agreement with (Larson and Weber) [25],(Penuela and Barceló)[26]

The activation energies calculated by Arrhenious plots are 28.7, 30.8 and 22.59 KJ/Mole for propanil degradation in river, tap and distilled waters and the results are given in table 4. The effect of temperatures on rate of photodegradation of propanil in tap water is shown in Figure 2.

UV-Visible spectrophotometric method was used to monitor the formation of photodegradation products at various time of irradiation during the photolysis of propanil in ZnO suspension water. Absorption spectrum of propanil in distilled, tap and river waters containing ZnO were determined and their wavelengths with molar absorptivity are listed in Table 5.

The value quantum yield for Propanil Degradation in Different Type Water were 0.31 in distilled water. A review in literature on the measurement of quantum yield in heterogeneous photo-catalyst system shows the majority of papers that report the quantum yield as apparent quantum yield .However Sarpone [27, 28] has recently reported the possibility of determination of the true quantum yield in heterogeneous photo-catalyst system by calculation of actual number of photons absorbed by the photocatalyst. Al -Yassiri and co workers[29], determined the quantum yield for
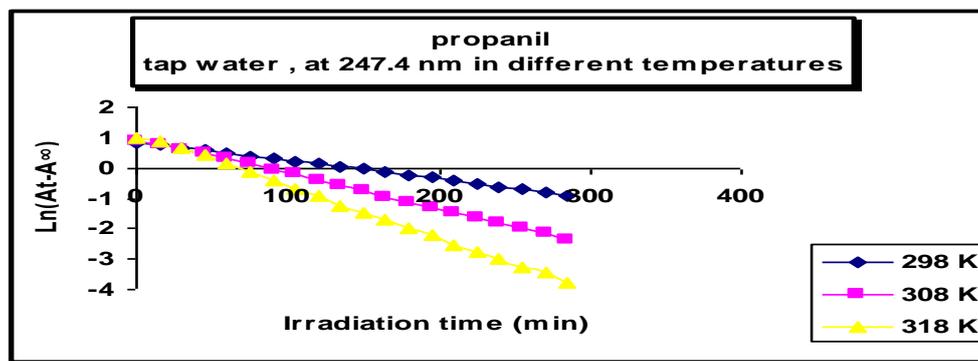
Fig-2: Effect of temperature on rate of photodegradation of propanil in tap water (initial concentration of propanil 10^{-4} M, ZnO loading of 0.4 g/l and oxygen flow rate of 20 ml/min).

photocatalyst degradation of DDVP, the value was obtained about 0.0571. The quantum yield for photocatalyst degradation of carbazyl was 0.18[30].

**Table-5:** Wavelengths and molar absorptivity of propanil in different types of waters

Sample of water	λ_{max} (nm)	ϵ_{max} L/mole.cm	λ_{max} (nm)	ϵ_{max} L/mole.cm	λ_{max} (nm)	ϵ_{max} L/mole.cm
Distilled	347.0	480	248.0	24130	210.0	29280
Tap	335.8	310	247.4	22970	210.0	28310
River	337.8	260	246.4	22920	214.8	23560

During the photolysis process in distilled water, the absorption bands at 248 and 210 nm were found to be decreased in intensity and shift to 250 nm which is belongs to 3,4-dichloroaniline. The formation of 3,4-dichloroaniline was checked by standard 3,4-dichloroaniline. Figure 3 shows the spectra of propanil degradation in distilled water containing ZnO and the irradiation time range 0 – 300 min.
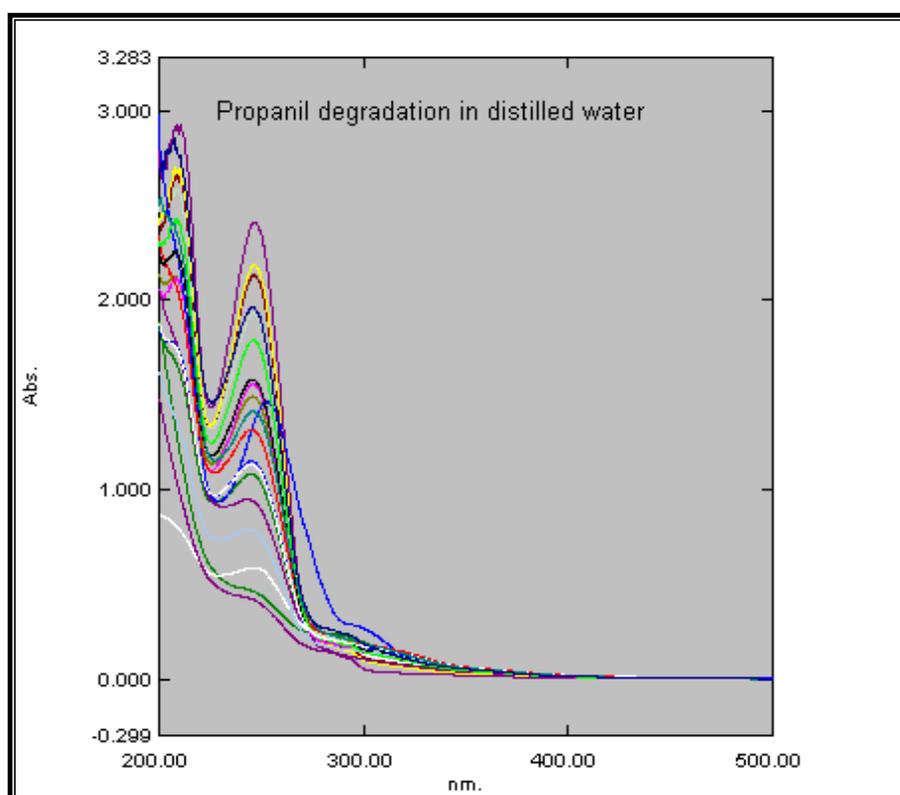
Fig-3: UV-Visible spectra change of degradation of propanil (10^{-4} M) in distilled water at irradiation time from 0 to 300 min

The spectra of degradation of propanil in tap and river waters were also determined by UV-Visible spectrophotometer. The study was carried out by using HPLC method for photodegradation of propanil using a column C18 (25 cm x 4.6 mm), eluent of 65/35 ml methanol/water, flow rate 1.0 ml/min and detect by UV at 254 nm. The HPLC chromatogram Figure-4 showed the absorption peak for propanil at 7.8 min and the intensity of the peak was decreased with irradiation time. New peaks were obtained during the irradiation of propanil, Test analysis of authentic compound
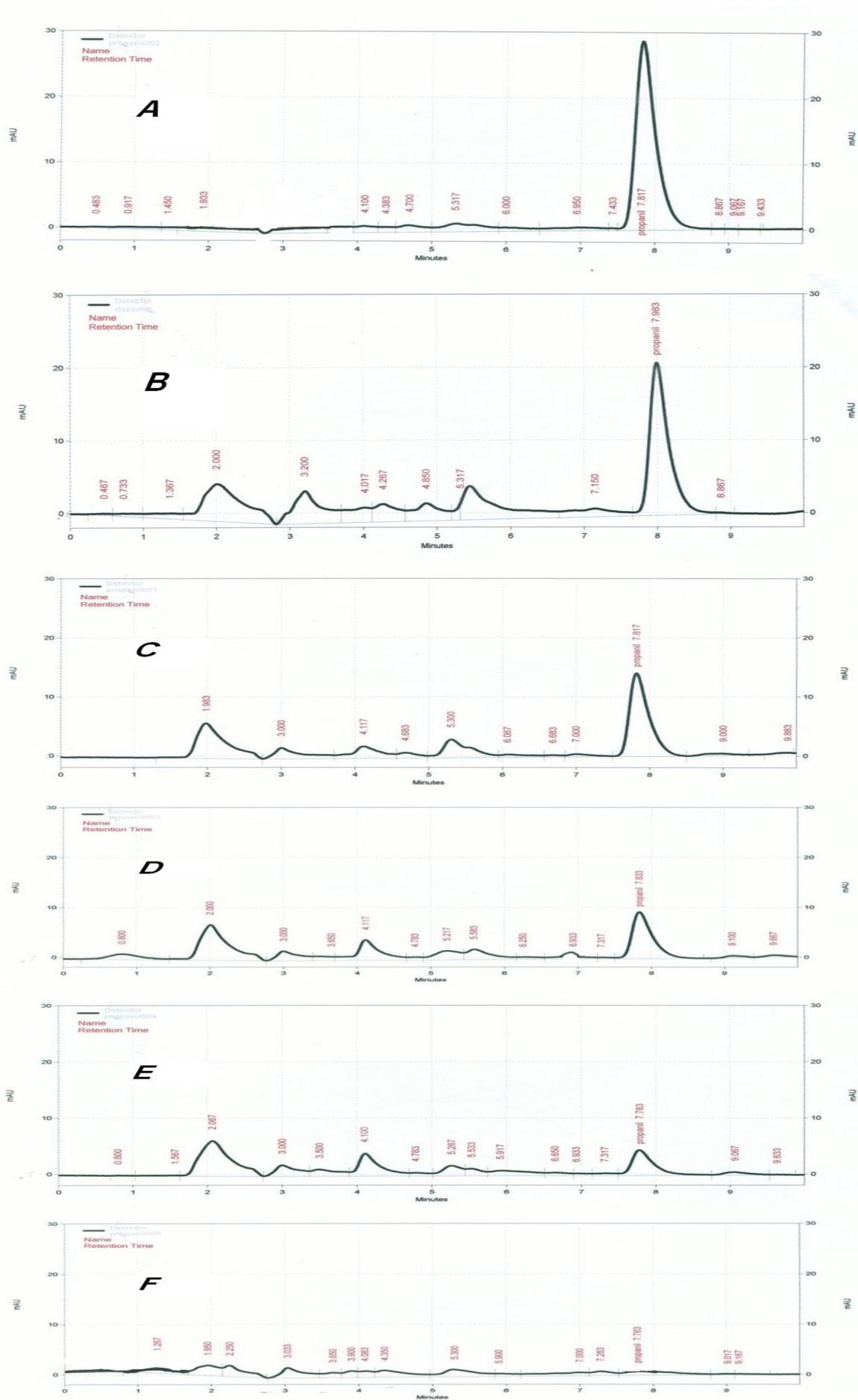
Fig-4: HPLC Chromatogram of Propanil [Solution (A) before Photolysis (B) after60 min(C) after120min (D) after180min (E) after240min (F) after300min] Irradiation. Initial Propanil Concentration is 10^{-4} M, ZnO Loading is 0.4g/l and Oxygen Flow Rate 10ml/min. The HPLC Condition are: Mobile Phase Methanol: Water (65/35V/V) Colume25cm x4.6mmC$_{18}$and UV. Detector at 254 nm.

after one hours reveals that new peak was related to propanoic acid at 3.2 min and after 2 hours a anew peak was noticed at 5.3 min which is belong to 3,4-dichloroaniline and after 3 hours a peak at 6.8 min belongs to 4-chloroanoline,After four hours of irradiation the prondpanil peak continue to decrease and also the primary products peak starts to decrease and After 5 hours of irradiation, a complete disappears of propanil peak which means all propanil was degradate. These results are in good agreements with the results obtained from UV-Visible spectrophotometric method.

3.1 *Proposed Mechanism for Photodegration of Propanil*

From the experimental results already discussed with the identification of the intermediates and the final photolytic products, one can suggest the mechanism of the photocatalytic oxidative reaction of propanil. When the semiconductor ZnO are illuminated with energy greater than band gap energy E_g, exited high-energy states of electron and hole pairs (e^-/h^+) are produced[31], the irradiation of semiconductor ZnO dispersions are summarized by reactions(1-5).

$$ZnO + hv \longrightarrow h^+_{vb} + e^-_{cb} \quad\dots\dots\dots\dots\dots\dots\dots\dots \quad (1)$$

$$H_2O + h^+_{vb} \longrightarrow \cdot OH + H^+ \quad\dots\dots\dots\dots\dots\dots\dots \quad (2)$$

$$H^+ + e^-_{cb} \longrightarrow \cdot H \quad\dots\dots\dots\dots\dots\dots\dots\dots \quad (3)$$

$$O_2 + e^-_{cb} \longrightarrow O_2 \cdot^- \xrightarrow{H^+} HO\cdot_2 \quad\dots\dots\dots\dots\dots\dots \quad (4)$$

$$2HO\cdot_2 \longrightarrow O_2 + H_2O_2 \xrightarrow{O_2\cdot} \cdot OH + {}^-OH + O_2 \dots\dots(5)$$

Where (C_b) and (V_b) represent conduction and valance band, respectively. The $\cdot$OH and HO$\cdot_2$ radicals can subsequently undergo series of reactions with propanil, leading to products summarized in the scheme illustrated in the scheme (1).
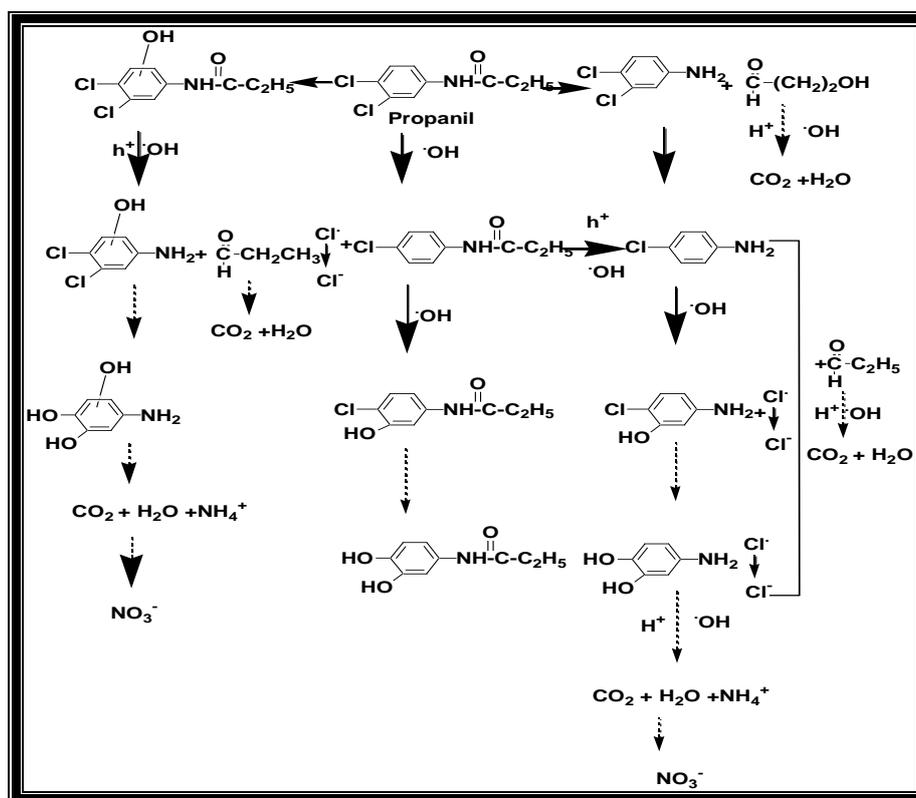
Scheme-1: The Proposed Intermediate Compounds in the Photodegradation of Propanil

4. CONCLUSION

From this experimental study, several conclusions can be made:

Propanil decomposition rate increases with the ZnO suspension concentration up to (0.4) g/L, then decrease with increasing ZnO suspension concentration. A kinetic model has been developed to successfully correlate the initial rates at varying ZnO suspension concentrations.

In the absence of UV irradiation, propanil cannot be decomposed by the ZnO suspension. The decomposition rate increases with the UV Power intensity but cannot further increase the decomposition rate in dark.

The results of the photodegradation of propanilas indicated by measurement of the increase in chloride ions concentration, conductivity and pH in aqueous medium.

The photodegradation rates propanilin three type waters followed first order kinetics and were in general greater compared to those measured in distilled water, showing a strong dependence on the constitution of the irradiated media especially on the dissolved organic matter and the salinity. The major photoproducts identified using UV, HPLC and other techniques.

The river water is the best aqueous medium for the photodegradation of propanil

The photocatalysis degradation of propanilis increasing by passing the humid oxygen.

The increasing of reaction temperature in the presence of ZnO raises the photodegradation rate of propanil

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