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ORIGINAL ARTICLE

Kinetic studies of catalytic photodegradation of chlorpyrifos insecticide in various natural waters

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Abstract The photocatalytic transformation of the insecticide chlorpyrifos O,O-diethyl-*O*-(3,5,6-trichloro-2-pyridinyl) phosphorothioate have been studied in different types of natural waters such as lake, river, ground as well as in distilled and drinking water under natural sun light and simulated irradiation sources. Physico-chemical properties of the natural water were determined which were chosen as the major indicators (namely pH, electric conductivity, turbidity, Cl^-, Na^+, K^+, NO_3^-, SO_4^{2-}, PO_4^{3-} and NH_4^+). Kinetic experiments were monitored using high performance liquid chromatography connected with UV-spectrophotometer detector. It was found that the photocatalytic degradation in all systems used in this work exhibited pseudo-first-order kinetics. The degradation rate constants were always higher for the heterogeneous catalysis in a system (TiO_2/UV) compared to the systems (radiation alone, TiO_2/visible or TiO_2/sun).

1. Introduction

Among the various organic substances, which are known as water pollutants, pesticides are a major pollution source for both underground and surface waters (Coupe and Blomquist, 2004). Chlorpyrifos is an organophosphorous insecticide widely used for urban and domestic pest control, including turf maintenance. It enters freshwater and saltwater ecosystems primarily as spray drift (Environmental Protection Agency, 1986).

Photocatalytic oxidation is considered as promising technology for the elimination of toxic organic pollutants. Investigations of the photocatalytic oxidation of pesticides in aqueous media irradiated by UV radiation have been a rapidly growing field of research (Kohler et al., 2002). Recently interest has been focused on the use of semiconductor materials as photocatalysts for the removal of organic and inorganic species from aqueous (Shiller et al., 2006).

One of the most effective methods for elimination of many hazardous, toxic, organic pollutants from the environment and particularly from wastewater is their photocatalytic degradation in the presence of catalyst particles (Buscaa et al., 2008). Among various semiconducting materials (sulfides, oxides, etc.) most attention has been given to TiO_2 due to its high photocatalytic activity, low cost, non-toxicity and high stability in aqueous solution (Hermann, 1999). TiO_2 as a

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photocatalyst may also improve under sunlight illumination (Pelentridou et al., 2008).

Many workers have reported on pesticide photodecomposition under a variety of irradiation conditions and different solutions. Most of these works use artificial solar sources of irradiation (xenon arc lamps or mercury lamps) or ultraviolet (UV) light combined with TiO_2 catalyst particles (Alves et al., 2006; Kralj et al., 2007; Muszkat et al., 1995). The photocatalytic degradation of some pesticides was studied in different natural waters (sea, river and lake) as well as in distilled water under natural sunlight and simulated irradiation (Konstantinou et al., 2001; Pehkonen and Zhang, 2002).

In the present work, photodegradation of chlorpyrifos in aqueous suspensions investigated using suspension TiO_2, as a photocatalyst under different types of light. The aim of this work was to investigate the influence of natural water on the kinetic degradation process. No such work has been done in Erbil-Kurdistan/Iraq.

2. Experimental

2.1. Reagents and solutions

Analytical reagent grade chemicals were employed for the preparation of all solutions. Methanol was HPLC grade and purchased from Tedia Company – USA. Chloroprifose was grade and purchased from Aldrich. The chemical structures and physico-chemical properties of the pesticide are shown below.

Name (CAS): O,O-diethyl-*O*-(3,5,6-trichloro-2-pyridinyl) phosphorothioate.
Common name: Chlorpyrifos.
Molecular formula: $C_9H_{11}C_{13}NO_3PS$.
Molecular weight: 350.5.
Melting point: 42–43.5 °C.
Vapour pressure: 2.7 mPa at 25 °C.
Water solubility: 1.4 mg/L at 25 °C.
Partition coefficient: Pow = 50,000; $\log P = 4.7$ (*n*-octanol/water).

2.2. Sample collection and physico-chemical properties of water

1. River water is taken from Greater-Zab River (45 km west Erbil City) in June 2008, temperature 32 °C.
2. Lake water is taken from Dwkan Lake (150 km East-Erbil City) in August 2008, temperature 42 °C.
3. Ground water is taken from the well around Erbil City in October 2008, temperature 25 °C.
4. Drinking water is taken from laboratory tap water.
5. Distilled water.

Water samples were collected in pre-washed polyethylene bottles. pH and electrical conductivity of the samples were measured while collecting the samples. Samples for sulfate and phosphate were refrigerated and analyzed within 24 h (Islam et al., 2007). The determined physico-chemical properties of natural water are shown in Table 1. All assays was carried out at least three times and the means of all the values were calculated (Adekunle et al., 2007).

2.3. Instrument and apparatus

pH was measured by using portable pH meter (HANNA instrument model PHB) with combined electrode. Electric conductivity (EC) was determined by conductivity meter Hi8314. Sodium and potassium ions were measured by flame photometer model Jenway PEP7 England (UK). Turbidity (Turb) was measured by turbidity meter Hf Scientific, Inc. model BRF 15CE. Hitachi L-4500 diode array HPLC connected with UV–Vis spectrophotometer detector and analytical column (PRT 720041, ET2501814 Nucleosil 120-5 C18 Machereg) was used for the determination of the concentration of chlorpyrifos during the photodegradation process with the mobile phase: 40% methanol 60% water, flow rate: 1.2 ml $\min^{-1}$, detector wavelength: 228 nm and injection volume: 20 µl (Morris and Therivel, 2001).

2.4. Photodegradation procedure

The photodegradation experiments were carried out at room temperature (30 °C) in a laboratory-made photoreactor (as shown in Fig. 1) including a 35 ml cylindrical photochemical cell. Twenty millilitres of solution (5 mg/L of chlorpyrifos dissolved in a small amount of methanol and completed the volume by water samples) was added to the photochemical cell then irradiated immediately by 100-Hg UV lamp (230 V, 50 Hz and 1 Am without selector) or visible light (tungsten lamp 500w).

For catalytic photodegradation, 0.2 g/L TiO_2 was used as a photocatalyst, the reaction mixture was stirred magnetically in the photoreaction cell and irradiated by radiation. The experiments of sunlight photodegradation were carried out under clear sky conditions. Incident solar radiation was measured within the wavelength of 285–2800 nm by (Solar 118-Haenni radio). The mean sunlight intensity was recorded from 603 to 729 Wm^{-2}.

3. Results and discussion

3.1. Direct photodegradation

Several experiments were made in order to know the influence of direct artificial and sunlight irradiation on the degradation

Table 1 Physico-chemical properties of natural water.

Water Sample	Turb.	pH	EC (µs cm^{-1})	NO_3^- (mg L^{-1})	SO_4^{-2} (mg L^{-1})	PO_4^{-3} (mg L^{-1})	SO_4^+ (mg L^{-1})	Cl^- (mg L^{-1})	Na^+ (mg L^{-1})	K^+ (mg L^{-1})
River water	13	7.9	250	5	142	0.05	0.19	6	11	3
Ground water	2	7.5	238	5	131	0.08	0.18	4	13	6
Lake water	4	7.8	241	4	139	0.04	0.2	3	16	4

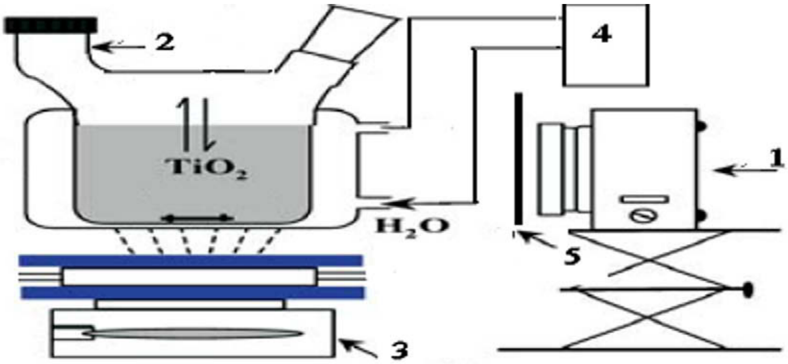

Figure 1 Block diagram of photodegradation reactor 1-sources of light 2-photochemical thermostat cell 3-stirrer 4-recycle water bath (water circulation).

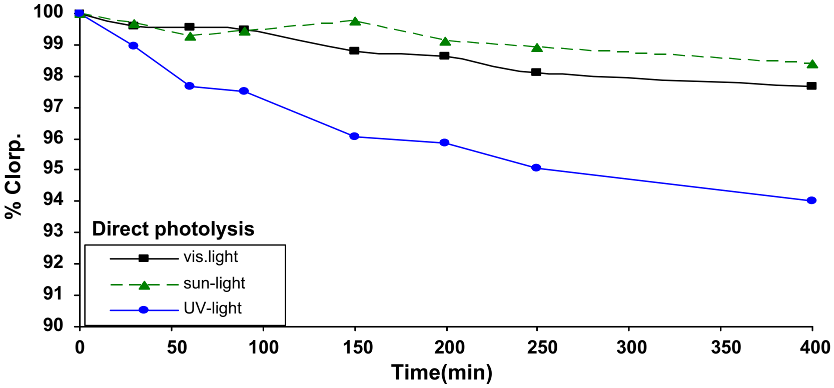

Figure 2 Direct photodegradation of chlorpyrifos under different types of radiation.

of chlorpyrifos solution without catalyst. Fig. 2 shows the effect of the different types of light (UV, visible and sunlight) on direct photodegradation of aqueous chlorpyrifos. The results in Fig. 2 indicate the very slow mineralization of chlorpyrifos under all types of light.

Results show that the photodegradation of samples exposed to the UV-light was faster than in those subjected to the direct sunlight or visible light. This is because, the emission spectra of UV-light mainly focuses on the ultraviolet band having the advantageous of short-wave emission and high energy to initiate photodegradation of compounds. However, the spectrum of sunlight ranged from ultraviolet to near infrared and with the main flux concentrated on the visible light band (Hemmateenejad et al., 2008).

3.2. Catalyst loading

The effect of the TiO_2 concentration (0.02–0.15 g/L) on the degradation percentage of chlorpyrifos was evaluated by using 5 mg/L of the substrate under UV-illumination after 60 min at room temperature as shown in Fig. 3. The results obtained verify that the degradation percentage of chlorpyrifos increases approximately with catalyst loading up to a concentration of 0.2 g/L. The enhancement is due to the increasing photon absorption by the photocatalyst. However, as the loading was increased beyond the optimum value, the degradation percentage decreased due to the opacity of the suspension and light scattering (Baran et al., 2008).

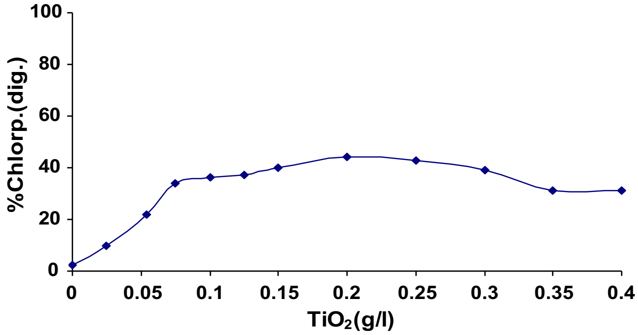

Figure 3 Effect of catalyst loading on the catalytic photodegradation of 5 ppm of chlorpyrifos.

3.3. Catalytic photodegradation

The catalytic photodegradation of chlorpyrifos was studied at four different experimental conditions: (1) under UV illumination with the presence of TiO_2, (2) under sunlight with the presence of TiO_2, (3) under visible-light illumination with the

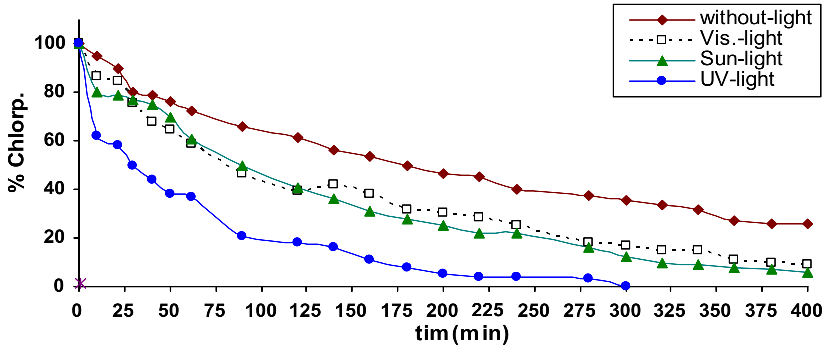

Figure 4 Catalytic photodegradation of chlorpyrifos under deferent types of radiation.

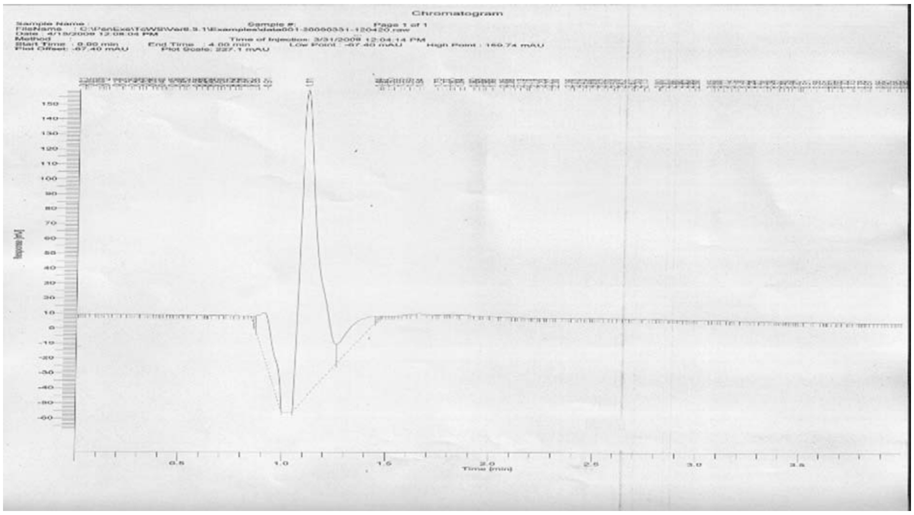

Figure 5 HPLC chromatogram of chlorpyrifos (5 ppm).

presence TiO_2 and (4) over TiO_2 with protection from light. The results of chlorpyrifos degradation under the above four conditions in distilled water have been shown in Fig. 4. It could be apparently seen in Fig. 4 that the presence of TiO_2 enhanced the degradation of chlorpyrifos under all types of light.

These results were similar to those obtained by Xin-Hong et al. (2006), who found that TiO_2/UV was much more efficient than using only UV lamps for 4-chloro phenol degradation, and similar to those obtained by Stylidi et al. (2003), who reported that Acid Orange was degraded much faster in the presence of TiO_2 and sunlight radiation than that in the absence of TiO_2. The higher efficiency of catalytic photodegradation in comparison with direct photodegradation of chlorpyrifos can be explained, as the photon energy in catalytic photodegradation is adapted to the absorption by the catalyst, not to the reactants. Their activation of the process goes through the excitation of the catalyst, but not through that of the reactants. This means that the light photons increase the activity of TiO_2 as a catalyst (Xin-Hong et al., 2006).

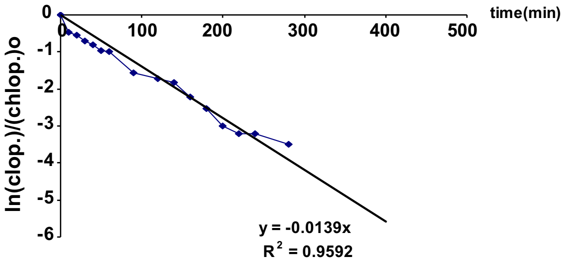

Figure 6 Plotting of ln [clop]/[chlop]$_0$ versus time of catalytic photodegradation over TiO_2/UV in distilled water.

3.4. Kinetic studies

The HPLC is a good technique to monitor the change in the concentration of chlorpyrifos in water (Gamiz-Gracia et al., 2005). The concentrations of chlorpyrifos during the catalytic photodegradation were monitored by observing the intensity of the peak height of retention time 1.1 min for chlorpyrifos, as shown in Fig. 5. The intensities of this peak decreased gradually during the degradation process reflecting the degradation of chlorpyrifos.

Graphical method was employed to predict the order of the degradation reactions. The plot of ln [chlop]/[chlop]° (where, [chlop] is the concentration of chlorpyrifos at time (t), [chlop]° is the initial concentration of chlorpyrifos), versus irradiant

Table 2 Reaction rate constant of direct and catalytic reaction photodgradation of chlorpyrifos in various types of water.

Types of water	Systems						
	Sun/w.c*	Vis/w.c	UV/w.c	Dark/TiO_2	Sun/TiO_2	Vis/TiO_2	UV/TiO_2
Lake water k (R^2)	0.00033 (0.81)	0.000190 (0.939)	0.000771 (0.890)	0.00334 (0.948)	0.00653 (0.882)	0.00597 (0.957)	*0.0117 (0.960)*
Ground water k (R^2)	0.00028 (0.861)	0.000184 (0.948)	0.00078 (0.894)	0.00362 (0.979)	0.00713 (0.9220)	0.00586 (0.892)	*0.0112 (0.84)*
River water k (R^2)	0.00031 (0.869)	0.000192 (0.972)	0.000791 (0.864)	0.00343 (0.954)	0.00692 (0.941)	0.00522 (0.902)	*0.0097 (0.904)*
Drinking water k (R^2)	0.00031 (0.874)	0.000182 (0.910)	0.000810 (0.883)	0.00301 (0.981)	0.00644 (0.939)	0.00519 (0.830)	*0.0095 (0.921)*
Distilled water k (R^2)	*0.00032 (0.9591)*	*0.00025 (0.8161)*	*0.000814 (0.9269)*	*0.00369 (0.9771)*	*0.00721 (0.994)*	*0.00601 (0.9454)*	*0.0139 (0.9592)*

* Without catalyst.

time shows a straight line behavior (see Fig. 6). This suggests the first-order kinetics of the catalytic photodegradation processes. The reaction rate constants (k) were determined from the slope of the straight line (Zhaoa et al., 2004). The direct and catalytic photodegradation kinetics data of chlorpyrifos shows the first-order reaction rate in all systems used in this work. Tables 2 and 3 show the values of k and $t_{1/2}$ determined from the direct and catalytic photodegradation process in different types of water.

3.5. Monitoring of chloride ion and conductivity during the degradation process

The chloride ions liberated after degradation of chlorpyrifos under different types of radiation source and in dark were determined quantitatively. The results in Fig. 7 show the formation of chloride ions during the degradation process continuously, showing that dechlorination was taking place (Schwack and Flober-Muller, 1990).

Table 3 Half life of direct and catalytic photodgradation reaction of chlorpyrifos in various types of water.

Types of water	Systems						
	Sun/w.c*	Vis/w.c	UV/w.c	Dark/TiO_2	Sun/TiO_2	Vis/TiO_2	UV/TiO_2
Lake water $t_{1/2}$ (min)	2100	3647.368	898.8327	207.485	106.1256	116.0804	59.23077
Ground water $t_{1/2}$ (min)	2475	3766.304	888.4615	191.4365	97.19495	118.2594	61.875
River water $t_{1/2}$ (min)	2235.484	3609.375	876.1062	202.0408	100.1445	132.7586	71.4433
Drinking water $t_{1/2}$ (min)	2235.484	3807.692	855.5556	230.2326	107.6087	133.526	72.94737
Distilled water $t_{1/2}$ (min)	2165.625	2772	851.3514	187.8049	96.1165	115.3078	49.85612

* Without catalyst.

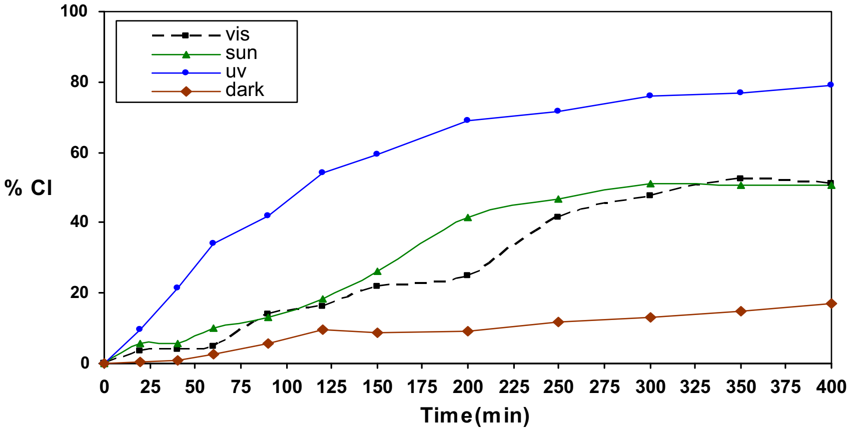

Figure 7 Cl% formed versus time through the catalytic photodegradation process of chlorpyrifos in distilled water.

The catalytic photodegradation was also monitored by measuring the change in solution conductivity. Conductivity changes (*Δ* cond.) of solution with times have been shown in Fig. 8. Results in this figure show that the conductivities of the solution are always increase with an increase of irradiation time. This increment in conductivity suggests that the organic substrate (chlorpyrifos and their degradation products) were converted to inorganic species. This certainly means that neutral organic molecules changed to conductive ionic species (Schwack and Flober-Muller, 1990).

3.6. Degradation of chlorpyrifos in different types of water

The direct photodegradation data of chlorpyrifos shows the first-order reaction rate carrier in all types of water. The results in Tables 2 and 3 show that the direct photodegradation rate of chlorpyrifos in natural and drinking water are nearly the same, as compared with the degradation rate in distilled water. The catalytic photodegradation of chlorpyrifos in different types of water also followed the first-order reaction (see Fig. 9). The results in Tables 2 and 3 are also indicating that the catalytic photodegradation of chlorpyrifos in natural waters (river, lake, ground and drinking waters) was lower than that in distilled water, and the agreement of these types of water according to catalytic photodegradation rate followed the following order: distilled water > ground water > lake water > river water > drinking water.

This may be due to the presence of organic carbon in natural water which inhibits the degradation rate of chlorpyrifos. These organic matters absorb most of the photons emitted thereby slowing down the degradation reaction of chlorpyrifos (Konstantinou et al., 2001). Also particulate matters such as sediment particles and microorganisms suspended in the water may scatter incident light, greatly reducing the penetration of light beneath the surface (Shiller et al., 2006).

However, the presence of inorganic ions has been shown to influence the kinetics and mechanism of the catalytic photodegradation process. It is well known that the catalytic photodegradation occurs at the surface of the semiconductor particles, so that the specific adsorption of ions may affect the system performance (Harir et al., 2008). The surface occupation by anions may be competitive with the adsorption of organic molecules, this effect being directly related to their coverage fraction. Inhibition by strongly adsorbed anions such

species[22].

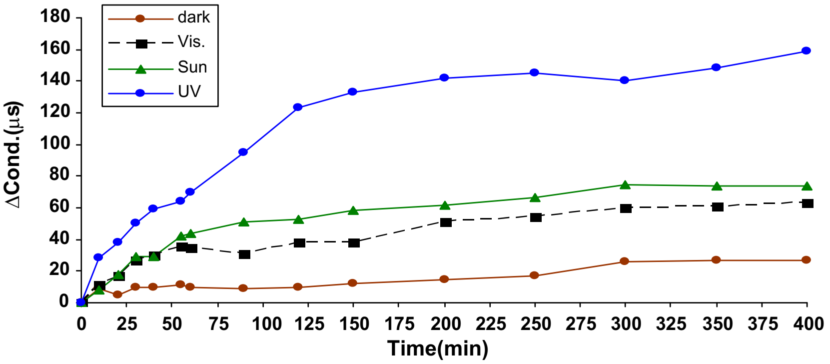

Figure 8 Conductivity changing versus time of through the catalytic photodegradation process of chlorpyrifos in distilled water.

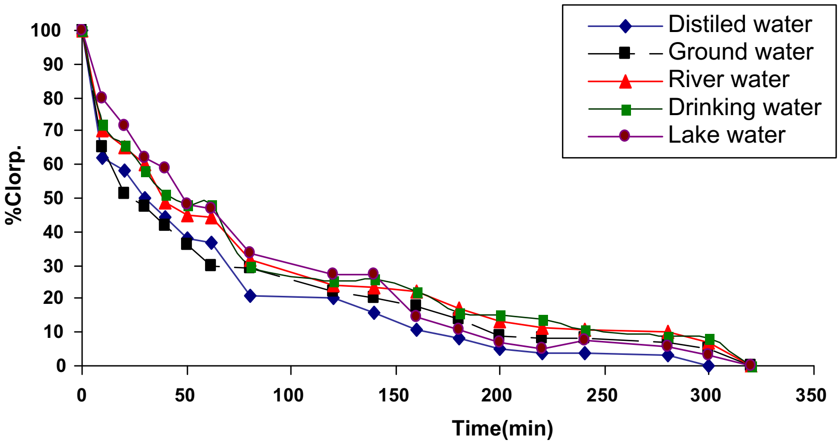

Figure 9 Catalytic photodegradation of chlorpyrifos under UV light radiation in different types of water.

as nitrate and perchlorate has been reported to have effected a negative on the catalytic photodegradation of organic compounds (Guillard et al., 2005).

4. Conclusions

Direct photodegradation has been shown not to be efficient systems for the degradation of chlorpyrifos. Therefore the catalytic photodegradation becomes necessary. The catalytic photodegradation over TiO_2 followed a pseudo-first-order reaction. The photocatalytic activity increases with an increase in catalyst concentration, and then it reaches an optimum value. At a concentration greater than the optimum, the activity decreased. UV-radiation used in this work was more efficient than sun or visible light as a source of radiation. In natural water samples, the rate of catalytic photodegradation of chlorpyrifos was lower than that in distilled water, and following the order: distilled water > ground water > lake water > river water > drinking water.

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