Treatment of Wastewater Contaminated with Pesticide (Alachlor) by Solar Enhanced Advanced Oxidation Processes

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ABSTRACT

The degradation performance of aqueous solution of pesticide Alachlor has been studied at solar pilot scale plant in two photocatalytic systems: homogeneous photocatalysis by photo-Fenton and heterogeneous photocatalysis with titanium dioxide. The pilot scale system included of compound parabolic collectors specially designed for solar photocatalytic applications, and installed at University of Baghdad, Department of Environmental Engineering back yard. The influence of different concentrations, H_2O_2 (200-2400 mg/l), Fe^{+2}(5- 30 mg/l) and TiO2 (100-500 mg/l) and their relationship with the degradation efficiency were studied.

The COD removal efficiency for homogeneous photocatalytic system at the best dosage was found to be 73.7%. The parent pollutant concentrations which were monitored using HPLC decreased to reach zero level at early time of the experiment. For heterogeneous photocatalytic system the COD removal efficiency was found to be 72.7%.

Key words: alachlor, advanced oxidation processes, photo-fenton, tio_2

معالجة المياه الملوثة بالمبيد (الاكلور) باستخدام عمليات الاكسدة المتقدمة المعززة بالطاقة الشمسية

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الخلاصة

تم دراسة تحلل المبيد (Alachlor) في المحاليل المائية باستخدام منظومة ريادية تعمل بنظام الاكسدة المتقدمة المتجانس (Homogeneous photocatalysis by photo-Fenton) ونظام الاكسدة المتقدمة الغير متجانس (Heterogeneous photocatalysis with titanium dioxide) باستخدام الطاقة الشمسية (compound parabolic collectors). تم دراسة تحلل المبيد تحت تاثير تراكيز مختلفة للمواد H_2O_2 (200-2400 mg/l) , Fe^{+2}(5- 30 mg/l) و TiO2 (100-500 mg/l). تم دراسة التحلل لتاثير (Fe^{+2}, H_2O_2) في النظام المتجانس و (TiO_2, H_2O_2) في النظام الغير متجانس, بلغت نسبة ازالة الCOD 73.7% في نظام الاكسدة المتجانسة و 72.7% في نظام الاكسدة الغير متجانسة.

الكلمات الرئيسية: الاكلور, الاكسدة المتقدمة, الفنتون–الضوئي, ثاني اوكسيد التيتانيوم.

1. INTRODUCTION

Continuing processes of industrialization and urbanization due to population growth, deforestation, and pollution are exerting pressure on the depleting freshwater resources in many parts of the world. A recent UN report mentions that the world's "freshwater is not being used sustainably" and calls for a "radical rethink" of policies to manage competing claims. The long-term sustainability of clean water supply is dictated by source water protection, management of water resources, and the efficiency of water reclamation from various effluents, **UN, 2012**.

The halogenated organic pesticide and/or a derivative probably entered natural aquatic environments concurrently with the development of the first manufacturing process. No doubt there was a waste disposal problem which led to a discharge into a river or some other body of water. Applying the pesticides on farms led also to the contamination of ground and surface water. Some evidence that potable, recreational, irrigational, fish, and shellfish waters were contaminated with pesticides began to appear in the literature about 1945. However, much of the early evidence was largely circumstantial as observed from physiological responses of aquatic organisms, **Faust, 1972**. Alachlor is a herbicide used for pre emergent control of broadleaf weeds and annual grasses in crops, mainly on corn and sorghum with a percent of about 57% and for soybeans with a percent of about 43%. Application to other yields like vegetables, cotton, peanuts and forage crops contributes to less than 1% of its use. The main source of its release to the environment is through manufacturing and use as a herbicide. It was detected in rural domestic well water through the national survey of pesticides in drinking water wells that conducted by the EPA. EPA's pesticides in ground water database reports that Alachlor is present in ground water at concentrations above the Minimum concentration level (MCL) in at least 15 States, the MCL in drinking water for Alachlor is 0.002 mg/l, **EPA, 2003**. As early as 1965, Stumm-Zollinger and Fair published a report, indicating that some organics are not completely eliminated by conventional wastewater treatment. At recent time, the presence of a high amount of emerging contaminants in MWTP effluents in various countries, confirm that the conventional treatment for these micro contaminants is ineffective, **Stumm, 1965**.

Advanced oxidation process (AOP) is used for various applications in wastewater treatment, water reclamation, indirect potable water reuse, drinking water production, and recently in micro-pollutant control of sewage treatment effluents, The advantage of AOPs is the relative high reaction power of hydroxyl radical. As a result of the high reaction power, reactions with $OH^{\bullet}$ radicals are very fast and nonselective, **Buxton, et al., 1988**.

AOPs can be classified by the way of generation of radicals. Three main classes are given: (1) direct generation of radicals by physically based processes, (2) generation of radicals by the addition of oxidants, and (3) generation of radicals by the use of solid catalysts, **Chong, et al., 2010**.

Mixtures of ferrous iron and hydrogen peroxide are called Fenton reagent Eq. (1), in the end the Fenton reaction comes to a quasi-standstill through the formation of stable iron complexes.

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^{-} + OH^{\bullet} \quad (1)$$

If light with a wavelength shorter than 580 nm is used, the formed iron complexes suffer photoreduction. The first step in this photoreduction is a ligand-to-metal charge-transfer (LMCT) reaction and as a consequence the intermediate complexes dissociate, **Zepp, et al., 1992**.

One of the outstanding advanced oxidation technologies is the photoexcitation of semiconductor surfaces with ultraviolet-visible radiation, which provides the appropriate band gap energies to generate photoactivated electron-hole pairs; electrons (e-) migrate to the conductivity band and holes (h+) are produced in the valance band Eq. (2), **Goslich, et al., 1997.**

$$TiO_2 + hv \rightarrow TiO_2(e^{-} + h^{+}) \quad (2)$$

After the formation of these (e^{-}– h^{+}) pairs, a recombination occurs in the catalyst, generating heat and adsorbing water molecules and hydroxyl ions present in the medium. These will act as electron donors, generating hydroxyl radicals in the hole (h^{+}) of the catalyst, Eq. (3) and Eq. (4), **Alfano, et al., 1997.**

$$h^{+} + H_2O \rightarrow OH^{\bullet} + h^{+} \quad (3)$$

$$h^{+} + OH^{-} \rightarrow OH^{\bullet} \quad (4)$$

Malato, et al., 2002, studied the performance of photocatalytic minerilization of four pesticides dissolved in water (formetanate, imidacloprid, diuron and methomyl) at pilot plant in two systems: heterogeneous system with TiO_2 and homogeneous system by photo-Fenton. The pilot plant is made up of (CPCs). Experimental conditions showed vanishing of pesticide and a comparison between the degrees of mineralisation that achieved in the two photocatalytic systems was held. The initial concentration tested with methomyl, formetanate and imidacloprid was 50 mg/l for each pesticide and for diuron it was 30 mg/l. The concentrations of the catalyst were 200 mg/l TiO_2 and 0.05mM iron. Total removal of the parent pesticides and 90% mineralisation have been achieved with all pesticides. Methomyl is the most hard to be degraded with both systems.

Oller, et al., 2006 studied the performance and technical feasibility of photocatalytic degradation of six pesticides dissolved in water (oxamyl, methomyl, cymoxanil, dimethoate, telone and pyrimethanil) at pilot plant using two systems: heterogeneous photocatalysis with TiO_2 and homogeneous photocatalysis using photo-Fenton processes. Heterogeneous tests were performed in solar pilot plant having three CPC units with a volume of 35 L under natural sunlight and a second solar pilot plant with four CPC units with a volume of 75 L was used for photo-Fenton photocatalysis tests. The studied initial pesticide concentration was 50 mg/l and the concentrations of the catalyst employed were 200 mg/l of TiO_2 and 20 mg/l of iron. Toxicity (*Vibrio fischeri*, Biofix) and biodegradability (Z–W) tests of the initial pesticide solutions were measured. Total degradation of the parent substances and about complete mineralization were achieved for all tested pesticides. homogeneous treatment was more efficient than heterogeneous, not only for pesticide degradation, but also for TOC mineralization, except for dimethoate for which the mineralization rate was quite similar in both photocatalyitic treatments.

The objective of this work is to get an idea about the effectiveness of solar AOPs in the degradation of Alachlor dissolved in water. The solar AOPs selected to carry out this study were; homogeneous solar photo-Fenton and heterogeneous solar photocatalysis. To achieve the experimental objective, different variables were chosen to be followed throughout the treatment: H_2O_2, Fe^{+2} and TiO_2 concentrations.

2. EXPERIMENTAL

2.1 Chemicals

The pesticide was in commercial form and bought from Hebei chinally international trade Co.LTD (china), the peurity Alachlor was 94%. The chemical structure is depicted in **Fig.1.** The physical and chemical properties of the pesticide are presented in **Table 1.**

H_2O_2 was from Hopkin and Williams with purity 35%. All the samples were prepared by dissolving requisite quantity in distilled water.

The pH of the solution was adjusted by using (H_2SO_4) and (NaOH) solution. $FeSO_4.7H_2O$ Was from Panreac with purity 99.9%. The Sulfuric acid was from Riedel-deHaën with purity 97%. Sodium hydroxide was from BDH with purity 99%. Titanium dioxide P25 was from HIMEDIA with purity 99%. Acetonitrile HPLC grade was from Sigma-Aldrich with purity 99.9%

2.2 Equipements

The pilot plant was installed at Baghdad University. The hydraulic circuit of the reactor consists of a tank, centrifugal re-circulation pump and solar collector, shown in **Fig.2** and **Fig.3**.

The plant is designed for operation in batch mode. The total volume of contaminated water in the experiments was (16 L) and the volume irradiated in the solar collector was (5 L). Solar collector consists of two Compound Parabolic Collectors (CPC) in series placed on fixed supports inclined 33° (latitude of Baghdad) with respect to the horizontal plane and facing south, this provides optimized performance. The CPC reflectors consist of stainless steel plates coated with aluminum foil. The photo reactor is made of two borosilicate glass tubes (inner diameter 46.4 mm, outer diameter 50.0mm and length 1.32m). The connecting tubing is made of PVC with 62.5mm diameter.

The samples were taken from the (16 liter) stainless steel tank for analysis. The reaction solution is continuously fed to the reactor from the stainless steel tank by means of centrifugal pump (Reshani pumps, China). The Flow rate was constant in all experiments (1.4 m^3/hr), which corresponds to turbulent flow inside the photoreactor. Flow meter (LZS Model, Flowtech, Turkey) with a range of (0.5-1.9 m^3/hr). The pH of the solution was monitored by using pH meter (WTW, INOLAB 72, Germany).

Global UV radiation, which is the driving force for the experiments in this work, was measured by UV ultraviolet radiometer model (UVA/B-850009), from Sper Scientific Electronics Co. LTD, Taiwan. The radiometer is a combination of a diffuser, filter and photodiode. The diffuser ensures that radiation can be incident from an optical angle and so determines a correct angular response. The filter determines the spectral response of the system to ensure that only deliberated radiation is measured. The photodiode generates a voltage output linearly proportional the number of incident photons.

2.3 Experimental Procedure

The procedure was performed as follows:

1. The solar reactor was cleaned and filled with distilled water to ensure that no other compounds were present in the reactor. Initially the solar collectors were covered to prevent any photochemical reactions and to study the performance of dark Fenton reactions.
2. The desired amount of pesticides were measured and diluted in distilled water. This solution was introduced in to the pilot plant. The pollutants treated have low to medium solubility, so the pollutants were re-circulated until perfect homogenization and pollutants dissolution was attained. The duration of this phase was (15-30) min.
3. The initial sample (sample 1) was taken and the pH value was adjusted immediately to 2.9 for homogeneous system to prevent sedimentation of iron species.
4. Ferrous sulphate was added in the desired concentrations. After mixing for 15 min the hydrogen peroxide was added at the desired concentrations to start the oxidation reaction.

   In the heterogeneous system, after the addition of the TiO_2, the mixing takes 45 min before the addition of hydrogen peroxide to ensure the adsorption of pollutants on the TiO_2 particles.
5. After the addition of H_2O_2, the circulation was continued for 15 min then the light protection was removed from the solar collectors. This is the moment in which the photo-Fenton degradation experiment begins.
6. Samples were taken after 15 min for homogeneous system and after 30 min for heterogeneous system.
7. Global UV irradiation was measured by the UV radiometer when each regular sample was taken.

2.4 Analysis

High Performance Liquid Chromatography (HPLC), PerkinElmer series 200, USA, was used to qualitative identification of the pesticide concentration and the intermediate compounds which evolve through the oxidation reaction. The analyses were carried out at flow rate 1(mL/min), wavelength was 225 nm, CAN/H_2O=60/40 with analytical column C18, 5 µm particle size, L*I.D. 25 cm*4.6mm.

Chemical Oxygen Demand of samples was analyzed by COD Photometer system (model RD-125, Lovibond Company, Germany).

2.5 Standarized treatment time

The average intensity of UV solar radiation varies with the time of the year, geographical location and with the atmospheric conditions, as a result, the photocatalytic treatment time was standardized based on a constant solar radiation intensity of 30W/m^2, which corresponds to the average intensity achieved in a clear sunny day, **Malato, et al., 2002**. The time t_{30W}, was calculated as follows:

$$t_{30w,i} = t_{30w,i-1} + \Delta t_n \frac{UV\ V_R}{30 V_T} \quad (5)$$

$$\Delta t_n = t_i - t_{i-1} \quad (6)$$

where Δt_n is the time interval between sampling, UV is the average UV solar intensity (W/m^2) during the sampling time interval, and V_R and V_T are the reactor and total (the volume of liquid in the entire system) liquid volumes, respectively. This approach allows the solar UV intensity which is independent of geographical location or the time of the year of the experiments, **Jiménez, et al., 2011**.

3. RESULTS AND DISCUSSION

3.1 Solar Homogeneous Photo- Fenton System

3.1.1 Effect of initial H_2O_2 concentration

The effect of H_2O_2 initial concentration (400, 800, 1200 and 1600 mg/l) on solar photo-Fenton process was tested to optimize the amount of H_2O_2 required to degraded Alachlor (ALC).

Fixed initial concentration of ALC=45 mg/l, initial amount of Fe^{+2} =20 mg/l and initial pH equal to 2.9 were maintained throughout the experiments. **Fig.4** shows the relation between the removal efficiency (COD mineralization efficiency) and the normalized illumination time t_{30}w for different initial concentration of H_2O_2.

At initial concentration of 400mg/l H_2O_2, the removal efficiency was obtained to be 38.9% only. As the concentration of H_2O_2 increased an improvement in the mineralization efficiency was noticed. H_2O_2 concentrations of 1200 mg/l and 1600 mg/l showed a removal efficiency of 71.3% and 73.7% respectively. The addition of excess amount of H_2O_2 will not increase the efficiency, a high concentration of H_2O_2 may behave as an $OH^\bullet$ radical scavenger, Therefore 1600 mg/l H_2O_2 was chosen as the best concentration for the mineralization of ALC.

The enhancement in the removal efficiency can be explained as: in the presence of Fe^{+2}, reactions between Fe^{+2} and H_2O_2 powered by solar irradiation leads to more $HO^{\bullet}$ radicals available to attack the pollutants structure and therefore the degradation increased.

Chong, et al., 2010 found that further addition of H_2O_2 will decrease the overall reaction rate, due to the formation of less penetrative $HO_2^{\bullet}$ radicals.

3.1.2 **Effect of initial Fe^{+2} concentrations**

The effect of initial Fe^{+2} concentrations on photo-Fenton process was tested by carrying out experiments with various amounts of Fe^{+2} (5, 10, 20 and 30 mg/l). The best H_2O_2 concentration (1600 mg/l) from the previous section was used in these experiments. The initial pH was maintained to be equal to 2.9.

Fig.5 shows the relation between the removal efficiency and the normalized illumination time $t_{30}w$ for different initial concentration of Fe^{+2}. It can be noticed that the degradation efficiency slightly increased by increasing the iron concentration, both Fe^{+2} concentrations of 20 mg/l and 30 mg/l showed nearly similar results for the mineralization efficiency which were 73.7% and 74.4% respectively, for that 20 mg/l was chosen to be the best concentration of Fe^{+2} in the mineralization treatment of ALC.

Iron causes turbidity and too high iron concentration generates dark zones in the photo reactor, which decreases the photo reactor efficiency, because part of the incident light does not enter the photo reactor but it is lost due to scattering, **Zapata et al., 2009**.

ALC concentration was measured and monitored using the HPLC analysis. ALC can be identified after retention time=6.8 min. The evolution of the intermediate products can be observed clearly from the chromatogram in **Fig.6** as the irradiation time was proceeds. Also it can be notice that a complete disappearance of ALC during the photo-Fenton treatment. Elimination of ALC was achieved after t=15min (t_{30w}=3min) of irradiation time while the intermediate products still appeared until the end of experiment.

3.2 Solar Heterogeneous Photocatalyst System

3.2.1 Effect of initial TiO_2 concentration

Heterogeneous photocatalysis experiments were applied to assess the feasibility of use TiO_2 in the degradation of ALC. Different concentrations of TiO_2 (100, 200, 300, 400 and 500 mg/l) were used. ALC concentration=45 mg/l, H_2O_2=1200 mg/l and pH =4.5.

Fig.7 shows the relation between the removal efficiency and the normalized illumination time (t_{30w}) for different initial concentration of TiO_2. The best result was obtained at 200 mg/l of TiO_2 with removal efficiency of 67.6%, above this concentration the degradation of ALC tend to decrease to reach 61% at 500 mg/l.

The increase in removal efficiency can be explained by the increase in the total surface area (or number of active sites) available for photocatalytic reaction as the dosage of TiO_2 increased. However, when TiO_2 was overdosed, the intensity of incident UV light was attenuated because of the decreased light penetration and increased light scattering, which embedded the positive effect coming from the dosage increment and therefore the overall performance reduced, **Eissa et al., 2009**. The tendency towards agglomeration (particle-particle interaction) also increases at high solids concentration, resulting in a reduction in catalyst surface area available for light absorption and hence a drop in the photocatalytic degradation rate, **Saber et al., 2011**.

3.2.2 Effect of adding H_2O_2

The effect of initial concentrations of H_2O_2 (800, 1200, 1600, 2000 and 2400 mg/l) on solar heterogeneous photocatalysis process were tested to optimize the amount of H_2O_2 required to degraded ALC. Fixed initial concentration of ALC=45 mg/l, initial amount of TiO_2=200 mg/l and initial pH = 4.5 were used.

Fig.8 shows the relation between the removal efficiency and the normalized illumination time t_{30w} for different initial concentration of H_2O_2. The best result was obtained at 2000 mg/l of H_2O_2 at removal efficiency of 73%.

The enhancement in the removal efficiency is due to the increase in the hydroxyl radical concentration. **Saber et al., 2011**, showed that addition of electron acceptors such as H_2O_2, would affect photocatalytic degradation of various pesticides and herbicides to enhance the formation of hydroxyl radicals as well as to inhibit electron/hole (e^-/h^+) pair recombination.

The increase in removal efficiency can be explained by increase the number of trapped electron in the electron/hole pairs and, consequently, avoid recombination and generate more $OH^\bullet$ for oxidizing species. It was expected that increasing the concentration of H_2O_2 reducing the rate of degradation due to the reaction of hydrogen peroxide with these radicals, and hence acts as an inhibiting agent.

4. CONCLUSIONS

The COD removal efficiency for homogeneous solar photocatalytic system at the optimal dosage 1600 mg/l H_2O_2, 20 mg/l Fe^{+2} at t_{30w}=15.8min was found to be 73.7% for Alachlor at initial concentration of 45 mg/l and pH=2.9. While the removal efficiency for hetrogeneous solar photocatalytic system at the optimal dosage 200 mg/l TiO_2, 2000 mg/l H_2O_2at t_{30w}=57.3min was found to be 72.7% for Alachlor at initial concentration of 45 mg/l and pH=4.5. Increasing the TiO_2, H_2O_2 or Fe^{+2} over the optimum amounts will decrease the removal efficiency. Biodegradability and toxicity tests during the photo-treatment couldn't be evaluated while it is important since some photo degradation by-products can be more dangerous and toxic than the original compounds.

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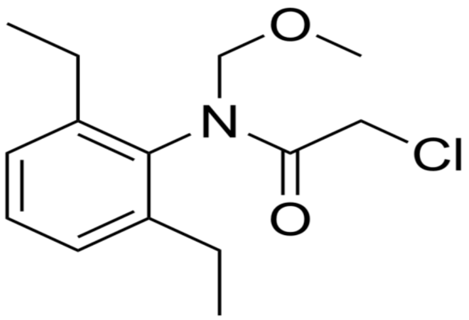

Figure 1. Chemical structure of Alachlor, **EPA, 2003.**

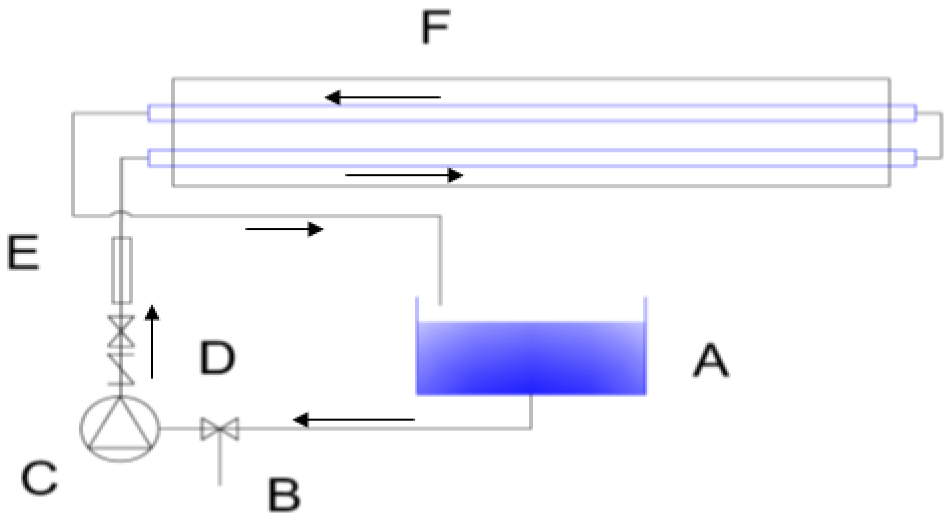

Figure 2. Schematic representation of the pilot plant (A) tank, (B) drain valve, (C) pump, (D) Valve, (E) flow meter, (F) solar collectors.

Figure 3. Photograph of the pilot plant.

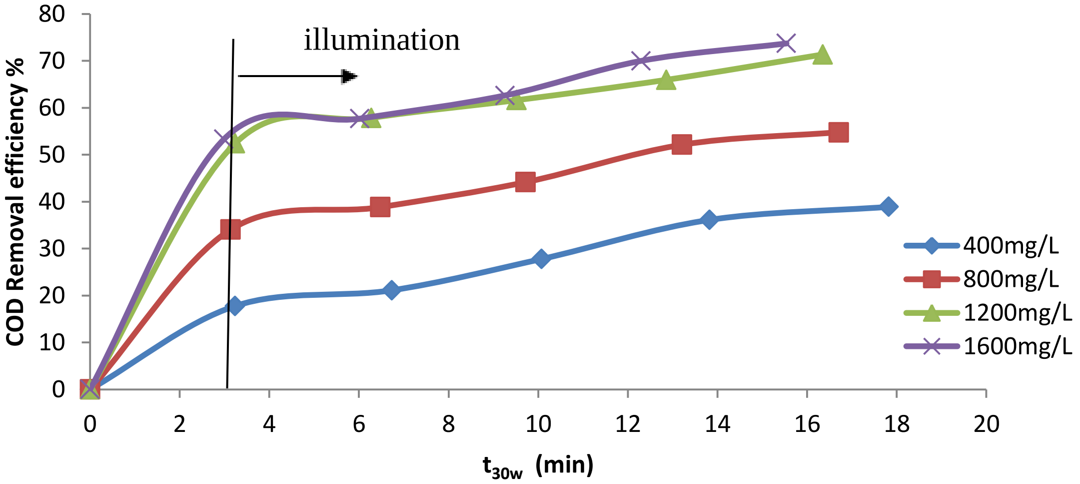

Figure 4. Effect of initial H_2O_2 concentrations on the COD mineralization of Alachlor by solar Photo- Fenton system at Alchlor conc.=45 mg/l , Fe^{+2} =20 mg/l and pH=2.9.

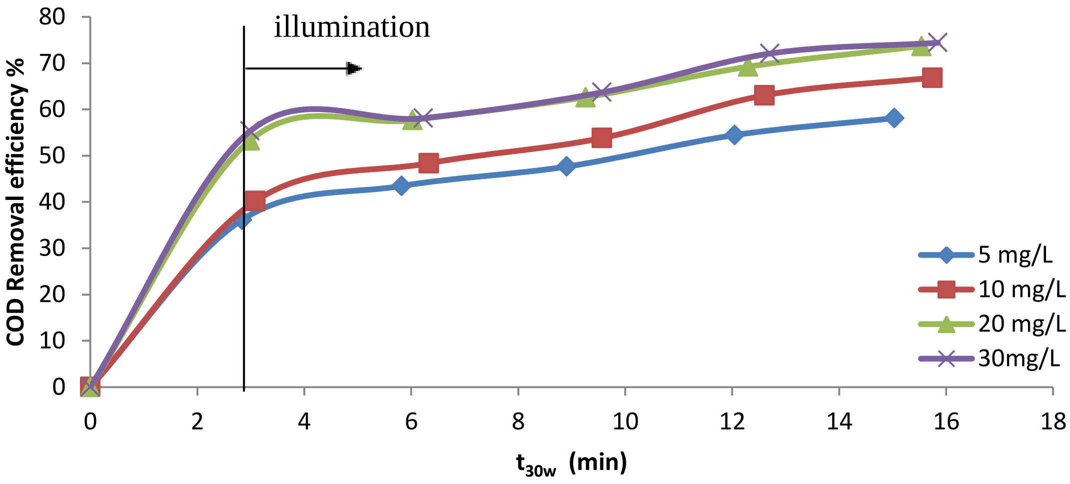

Figure 5. Effect of initial Fe^{+2} concentrations on the COD mineralization of Alachlor by solar photo-Fenton system at Alachlor conc.= 45 mg/l, H_2O_2=1600 mg/l and pH= 2.9.

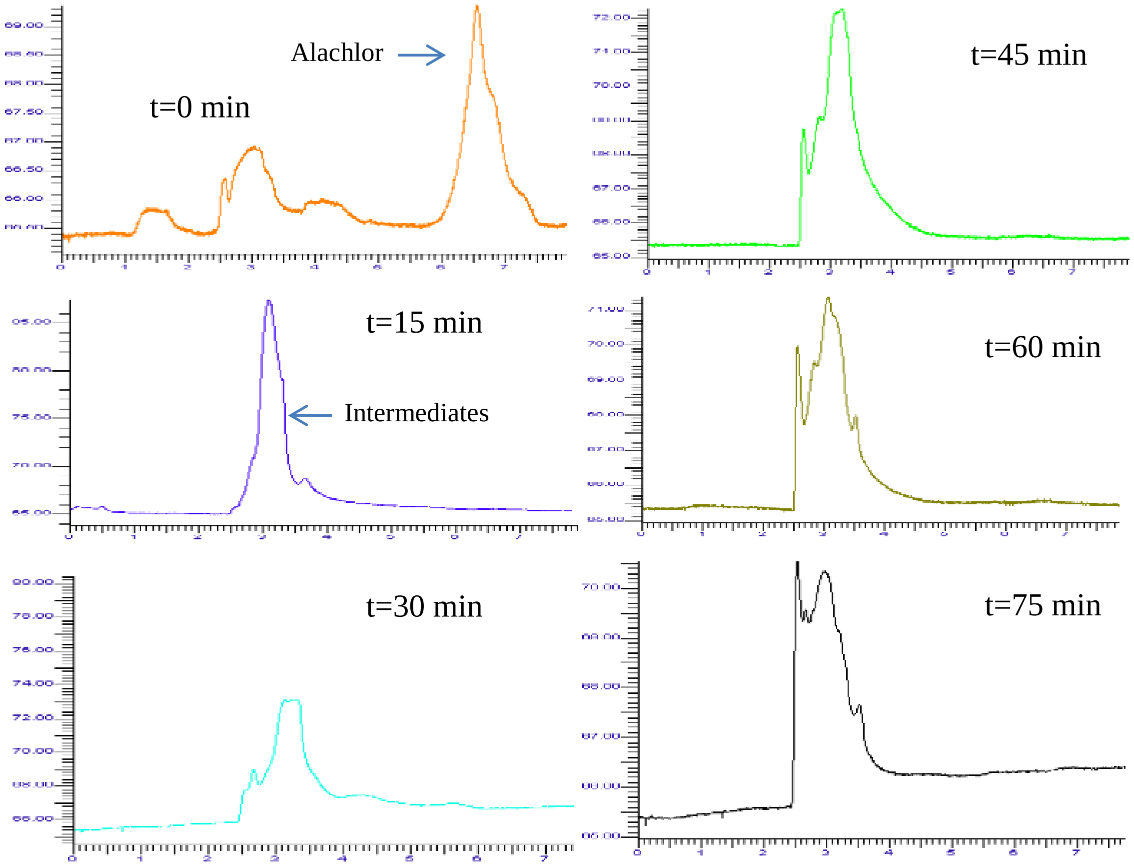

Figure 6. HPLC analysis for homogeneous photo-Fenton system, Alachlor=45 mg/l, H_2O_2=1600 mg/l, Fe^{+2}=20 mg/l and pH=2.9.

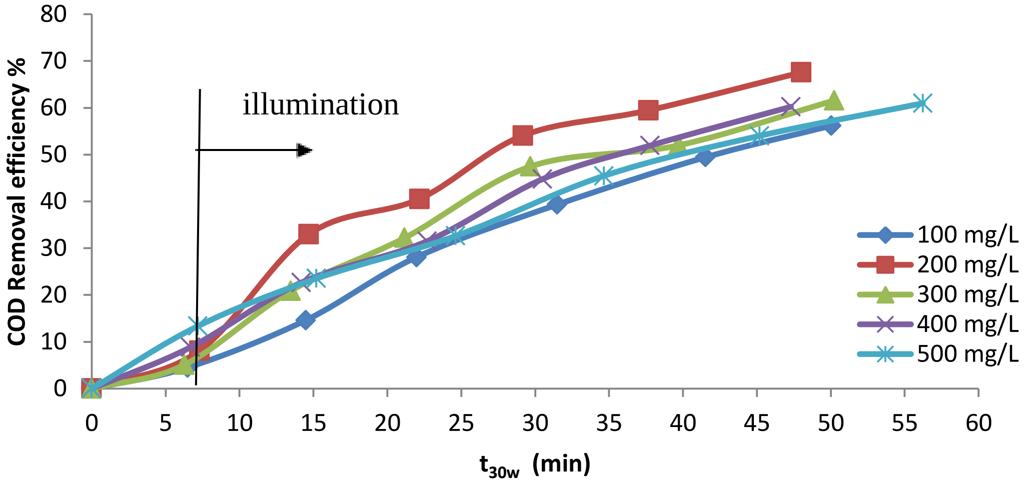

Figure 7. Effect of initial TiO_2 concentrations on the COD mineralization of Alachlor by heterogeneous solar photo-catalyst system, Alachlor conc.= 45 mg/l, H_2O_2= 1200 mg/l, pH=4.5.

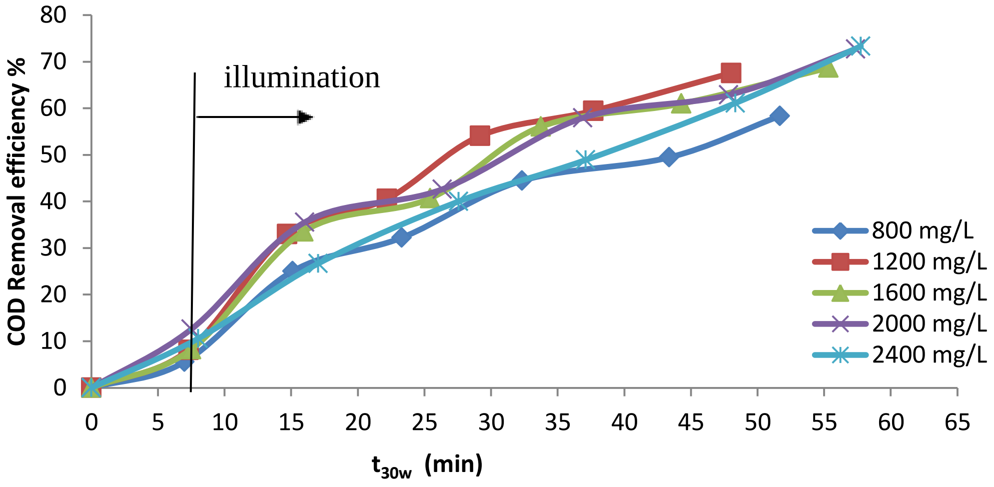

Figure 8. Effect of initial H_2O_2 concentrations on the COD mineralization of Alachlor by heterogeneous solar photocatalyst system at Alachlor conc.= 45 mg/l,TiO2=200 mg/l and pH=4.5.

Table 1.List of pesticides properties, **EPA, 2003**.

Formula	**$C_{14}H_{20}ClNO_2$**
Molar mass	269.767 g/mol
Solubility in water	140 mg/l at 23C°
Vapor Pressure	Negligible
Melting Point	40-41 C°
Kow	Log Kow = 2.63