Solar Photocatalytic Degradation of Diuron in Aqueous Solution by TiO$_2$

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ABSTRACT

The solar photocatalytic degradation of diuron, which is one of the herbicides, has been studied by a solar pilot plant in heterogeneous solar photocatalysis with titanium dioxide. The pilot plant was made up of compound parabolic collectors specially designed for solar photocatalytic applications. The influence of different variables such as, H$_2$O$_2$ initial concentration, TiO$_2$ initial concentration, and diuron initial concentration with their relationship to the degradation efficiency were studied. Hydrogen peroxide (H$_2$O$_2$) found to increase the rate of diuron degradation. The best removal efficiency of heterogeneous solar photocatalytic TiO$_2$ system was found to be 46.65 % and for heterogeneous solar photocatalytic TiO$_2$/ H$_2$O$_2$ system was found to be 80.65 %. Based on these results, the solar photocatalytic degradation by TiO$_2$/ H$_2$O$_2$ system could be a useful technology for the treatment of effluents containing diuron.

Keywords: Diuron, Photocatalyst, Titanium dioxide, solar, degradation

تحلل الدوران في محلول مائي بالتحفيز الضوئي بواسطة ثنائي أوكسيد التيتانيوم باستخدام الطاقة الشمسية

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الخلاصة

تمت دراسة التحلل بالتحفيز الضوئي للمبيد (ديورون - diuron) وهو أحد أنواع مبيدات الادغال/ الأعشاب بواسطة منظومة تعمل بنظام الاكسدة المتقدمة الغير متجانس (التحفيز الضوئي بثنائي أوكسيد التيتانيوم) باستخدام الطاقة الشمسية. تتكون المنظومة الريادية من مجمعات القطع المكافئ المركبة (compound parabolic collectors) مصممة خصيصا لتطبيقات التحفيز الضوئي بالطاقة الشمسية. درست تأثير المتغيرات المختلفة مثل التركيز الأولي لبيروكسيد الهيدروجين والتركيز الاولي لثنائي أوكسيد التيتانيوم والتركيز الاولي للمبيد وتأثيرها على كفاءة الازالة. وجد ان بيروكسيد الهيدروجين يزيد من معدل تحلل المبيد (ديورون). كانت أفضل كفاءة إزالة التحفيز الضوئي باستخدام نظام التحلل بواسطة ثنائي أوكسيد التيتانيوم لوحده تساوي 46.65 % وباستخدام نظام التحلل بواسطة ثنائي أوكسيد التيتانيوم مع بيروكسيد الهيدروجين كفاءة الازالة تساوي 80.65 %. بناء على هذه النتائج فان التحلل بالتحفيز الضوئي بواسطة الطاقة الشمسية باستخدام نظام ثنائي أوكسيد التيتانيوم مع بيروكسيد الهيدروجين يمكن ان تكون تكنولوجيا مفيدة لمعالجة المطروحات الحاوية على مبيد الديورون.

1. INTRODUCTION

Pollution of soils and aquatic systems by chemicals used in agriculture is one of the main present environmental problems. Diuron (*N*_-(3,4 dichlorophenyl)-*N,N*-dimethylurea), one of the most commonly used herbicides, belongs to the family of halogenophenylureas that represents an important class of contact herbicides applied in pre- and post-emergence to control broadleaf weeds in a wide variety of annual and perennial broadleaf and grass weeds **Field, et al.,1997, and Gooddy, et al., 2002**. Diuron is considered as highly toxic and persistent when applied in high dosages to the soil with a half-life of over 300 days **Malato, et al., 2011**. As a result, it is often detected in groundwater and surface water **Blanchoud, et al., 2004, Lapworth and Gooddy, 2006**. Diuron is suspected to be a carcinogenic and genotoxic compound **Revitt, et al., 2002**. Studies have also shown that it is toxic to photosynthetic organisms at concentrations levels of a few mgL^{-1} **Huang, et al., 2004, Rupp, et al., 2006**. Diuron is suspected to be a carcinogenic and genotoxic compound **Michaelidou and Nicolaou, 1996**. In this context, the development of technologies and management practices for the minimization of diuron is a necessary task.

Several researchers have developed an intensive effort of research on the chemical **Catalkaya and Kargi, 2007**, physicochemical **Bouras, et al., 2007**, photochemical **Malato, et al., 2009, Mazellier, et al., 1997**, heterogeneous photocatalytic **Macounová, et al., 2003**, **Bamba, et al., 2008**, electrochemical **Oturan, et al., 2008** and microbiological **Stasinakis, et al., 2006**, degradation methods of diuron, and the diuron transformation products. Especially, photocatalytic method (TiO_2) is highly promising because it can operate at ambient temperature and pressure with low energy photons.

In the present study, the degradation and mineralization of diuron in water using heterogeneous solar photocatalysis and heterogeneous solar photocatalysis with H_2O_2 and TiO_2 was investigated. The progress of mineralization of diuron was monitored by diuron concentrations.

2. EXPERIMENTAL
2.1 Reagents

Diuron was obtained from Fluka with 98.5% purity technical grade and was used as received. Titanium dioxide TiO_2 P25 (99 % purity (obtained from Fluka Co. Switzerland, with specific surface area of 50 m^2/g corresponding to the mean elementary particle size of 21±5 nm. Hydrogen peroxide H_2O_2 (reagent grade, 50% w/v) was obtained from Panreac Co., USA.

2.2 Equipment
2.2.1 Compound parabolic collectors (CPC) reactor

Compound parabolic pollectors (CPC) are static collectors with a reflective surface formed by two connected parabolic mirrors with an absorber tube in the focus and have been found to provide the most efficient light-harvesting optics for low concentrating systems, **Malato et al., 2009**. They support turbulent flow, have a closed system, are cheap and easy to maintain and as temperature does not play any significant role, there is no need for insulation.

A pilot plant was installed at Baghdad University / Department of Environmental Engineering backyard as shown in **Fig.1**. The hydraulic circuit of the reactor consists of a tank, centrifugal re-circulation pump, solar collector, connecting tubing and valves, **Fig.2**. The plant is designed for

operation in a batch mode. The total volume in the experiments is 20 L and the volume irradiated in the solar collector is 4.46 L.

The 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 the south , this provides optimized performance as agreed with **Al- Saqqar, 2000;** and **Mahdi et al., 2011**. The CPC reflectors consist of stainless steel plates coated with aluminum foil. The photoreactor is made of two borosilicate glass tubes with 46.4 mm inner diameter, 50.0 mm outer diameter and 1.32 m in length. The connecting tubing is made of PVC with 62.5mm in diameter.

The 20 L stainless steel tank provides aeration and samples for analysis. The solution is continuously fed to the plug flow reactor from the stainless steel tank by means of a centrifugal pump (Golden pumps, China). The flow rate was constant at ($1.5m^3$/hr) in all experiments, which corresponds to turbulent flow inside the photoreactor. Flow rate was adjusted by a flow meter (model LZS, Flowtech, Turkey. The pH of the solution was monitored by using a pH meter model (WTW, INOLAB 72, Germany). The pH value was chosen according   to previous work of Malato et al., 2009 and Bamba et al., 2008. They indicated that pH =5 is the optimal value for the heterogeneous solar photocatalysis with TiO2.

2.2.2 Radiometer

Global UV radiation, which is the driving force for the experiments in this work, was measured by UVA ultraviolet radiometer model (UVA-365) wave length 365nm ultraviolet, with three ranges 199.9 uW/cm^2,1.999 mW/cm^2 and 19.99 mW/ cm^2 , from Lutron Electronics Co. LTD, USA. The radiometer was inclined 33° (latitude of Baghdad) with respect to the horizontal plane and facing the south in the same way as the CPCs of solar pilot plant.

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.
2. The correct amounts of diuron were measured and diluted in distilled water. This solution was introduced to the pilot plant. The pollutants were re-circulated until perfect homogenization and pollutants dissolution were attained. The duration of this phase was (30) min.
3. The reagents were added in different concentrations related to the experiments, H_2O_2 (200 - 500 mg/L), and TiO_2 (200 - 500 mg/L).
4. Regular samples were drawn (each 30 minutes) to measure the main process variables.
5. Global UV irradiation was measured by the UV radiometer when each regular sample was taken.

The intensity of solar radiation depends on season, location, daytimes and weather. It's therefore more accurate to mathematically adjust the experiments by applying a correction factor as shown in Eqs.(1)and (2).

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

$$\Delta t_n = t_i - t_{i-1} \qquad (2)$$

Where t_n is the experimental time for each sample, UV is the average solar ultraviolet radiation measured between t_{n-1} and t_n where t_{30W} is the "normalized illumination time". In all experiments, time refers to a constant solar UV power of 30 W/m^2 which is nearly equivalent to the average UV power of a perfectly sunny day **Jiménez et al., 2011**.

2.4 Analysis
The analyses were performed in the laboratories of Environmental Engineering Department/ University of Baghdad. UV-vis spectrophotometer (Model T80 from PG Instrument Ltd, England), **Fig.3**, was used to measure the concentrations of diuron dissolved in water before and after treatment.

3. SOLAR HETEROGENEOUS PHOTOCATALYSIS
The heterogeneous solar photocatalytic detoxification process consists of making use of the near ultraviolet UV band of the solar spectrum (wavelength shorter than 400 nm), to photo-excite a semiconductor catalyst in contact with water and in the presence of oxygen, **Munter et al., 2001**.Semiconductors (e.g., TiO_2, ZnO, Fe_2O_3, CdS and ZnS) can act as sensitizers for light-induced redox processes due to their electronic structure, which is characterized by a filled valence band and an empty conduction band. Absorption of a photon of energy greater than the band gap energy leads to the formation of an electron/hole pair. The valence band holes are powerful oxidants depending on the semiconductor and pH. Most organic photodegradation reactions utilize the oxidizing power of the holes either directly or indirectly. In semiconductor electrodes only one species, either the hole or electron, is available for reaction due to band bending, while the complementary reaction takes place in the counter electrode, **Mills and Le Hunte, 1997**. **Fig. 4** shows a drawing, which is used to illustrate photocatalytic processes. It consists of a superposition of the energy bands of a generic semiconductor (valence band VB, conduction band CB) and the geometrical image of a particle, **Malato et al., 2009**.

Absorption of a photon with an energy hv greater than or equal to the band gap energy Eg generally leads to the formation of an electron/hole pair in the semiconductor particle. These charge carriers subsequently recombine and dissipate the input energy as heat, get trapped in metastable surface states, or react with electron donors and acceptors adsorbed on the surface or bound within the electrical double layer. Simultaneously, in the presence of a fluid (water), spontaneous adsorption occurs (water and pollutant) and according to the redox potential of each adsorbate, an electron transfer proceeds towards acceptor molecules, whereas a positive hole is transferred to a donor molecule. Since the photonic excitation of the catalyst appears at the initial step of the activation of the whole catalytic system, it is necessary that the photon has enough energy to be absorbed by the catalyst, not by the reactants. Subsequently, the activation of the process goes through the excitation of the solid but not through that of the reactants. It is well known that O_2 and water are essential for photooxidation, there is no degradation in the absence of either, **Byrne and Eggins, 1998**.

4. RESULTS AND DISCUSSIONS
4.1 Effect of Initial TiO$_2$ Concentration

Heterogeneous photocatalysis method is applied to assess the feasibility to use TiO$_2$ in the degradation of diuron. Different concentrations of TiO$_2$ (200, 300, 400 and 500 mg/L) were used. Diuron concentration =20 mg/L and pH =5.

Fig. 5 shows the relation between the degradation removal efficiency and the normalized illumination time t_{30w} for different initial concentrations of TiO$_2$. The best result was obtained at t_{30w} = 19 min, 400 mg/L of TiO$_2$ with removal efficiency of 46.65 %, above this concentration the degradation of diuron tends to decrease to reach 43.9% at 500 mg/L TiO$_2$. 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$_2$ is 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 was reduced. Therefore the optimum catalyst TiO$_2$ concentration has to be found in order to avoid excess catalyst and ensure total absorption of efficient photons, **Eissa et al.,** and **2009. Malato et al., 2011** stated that total disappearance of diuron was obtained at 75 min (t_{30w}) with initial concentration of diuron 22 mg/L, 200mg/L of TiO$_2$.

4.2 Effect of Adding H$_2$O$_2$

In this experiment, the possibility of increasing the removal efficiency of the heterogeneous photocatalysis was tested by adding different concentrations of H$_2$O$_2$ (200, 300, 400 and 500 mg/L). The optimum TiO$_2$ concentration 400 mg/L from the previous section was used in these experiments, the initial pH was equal to 5 and the concentration of diuron=20mg/L.

Fig. 6 shows the relation between the removal efficiency and the normalized illumination time t_{30W} for different initial concentrations of H$_2$O$_2$. An obvious positive influence on the degradation rates was observed by increasing the H$_2$O$_2$ concentration to 400mg/L, the removal efficiency was found to be 80.65 % at t_{30w} = 20.4 min. The increase in removal efficiency can be explained by increasing the number of trapped electrons in the electron/hole pairs and, consequently, avoiding recombination and generating more OH• for oxidizing species. It was expected that increasing the concentration of H2O2 reduces the rate of degradation due to the reaction of hydrogen peroxide   with   these   radicals,   and   hence   acts   as   an   inhibiting   agent.

5. CONCLUSIONS

1. TiO$_2$ photocatalyst was found to increase the photocatalytic activity for the degradation of diuron. The degradation rate was strongly affected by TiO$_2$ concentration.
2. It has been found that experiment with heterogeneous photocatalytic based on TiO$_2$ enhanced with H$_2$O$_2$ seems to give the best removal efficiency compared with TiO$_2$ alone experiments.
3. A complete mineralization cannot be attained due to the formation of the intermediates and the final products which are most difficult to degrade.
4. The advantages of TiO$_2$ photocatalytic process as an oxidative treatment are rapid degradation and simple handling. Therefore, this photocatalytic reaction would be applied to

wastewater treatment works as a new developing methodology for reducing levels of other pesticides and endocrine disrupting chemicals.

5. The best removal efficiency of heterogeneous solar photocatalytic TiO_2 system was found to be 46.65 % at t_{30W} = 19 min and for heterogeneous solar photocatalytic TiO_2/ H_2O_2 system was found to be 80.65 % at t_{30W} = 20.4 min.

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Figure 1. CPC at the backyard of the Environmental Engineering Department.
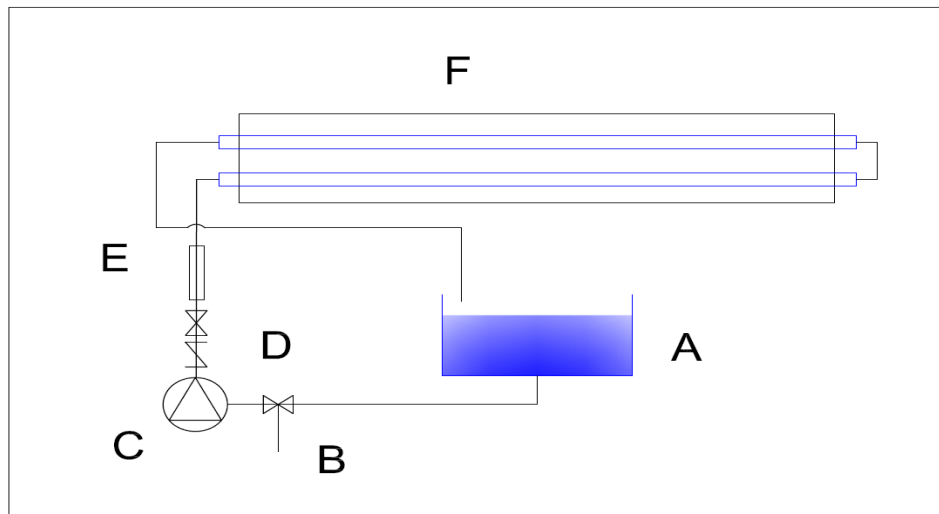
Figure2. Schematic representation of the pilot plant (A) tank, (B) drain valve, (C) pump, (D) valve, (E) flow meter and (F) solar collectors.
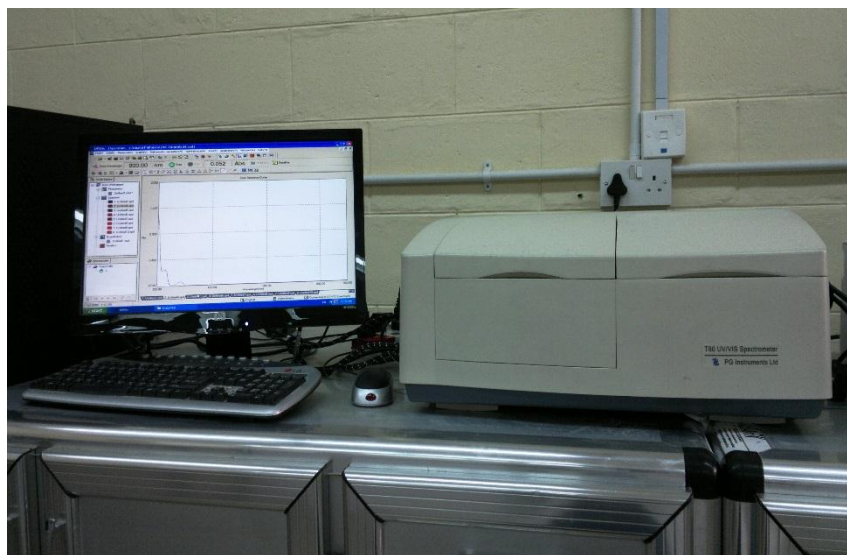

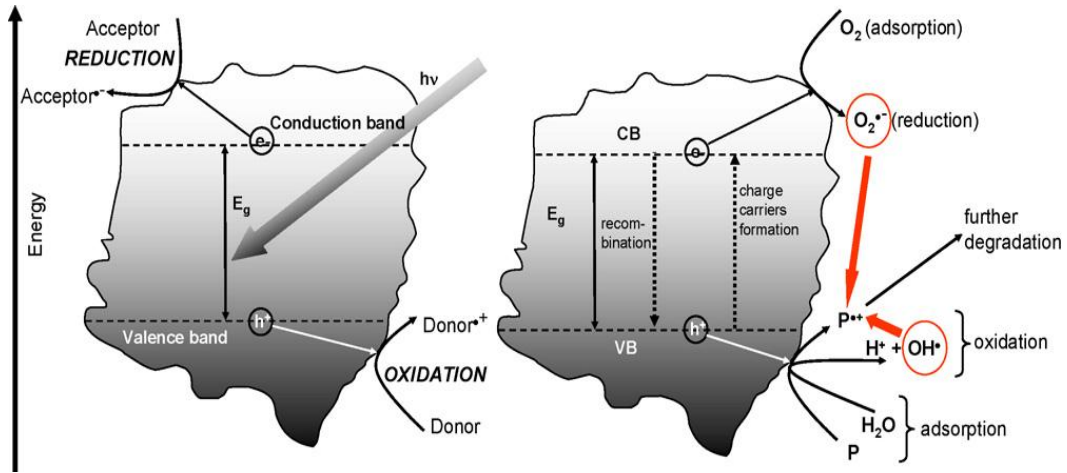**Figure 3.** UV- vis spectrophotometer.

Figure 4. Energy band diagram and fate of electrons and holes in a semiconductor particle in the presence of water containing a pollutant, **Malato et al., 2009**.
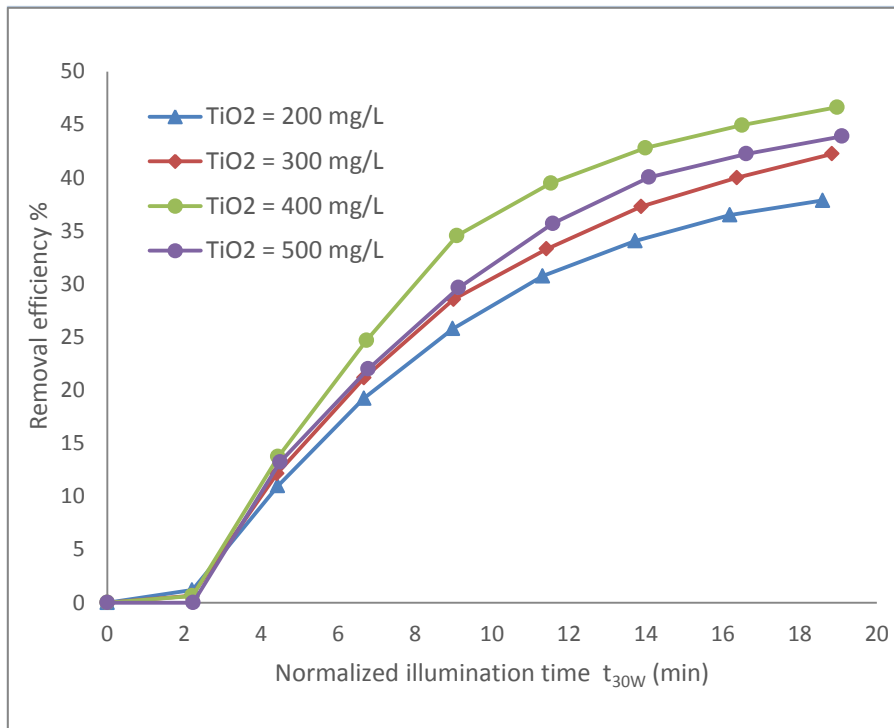

Figure 5. Effect of initial TiO_2 concentrations on the degradation of diuron by heterogeneous solar photocatalyst system, diuron conc.= 20 mg/L.
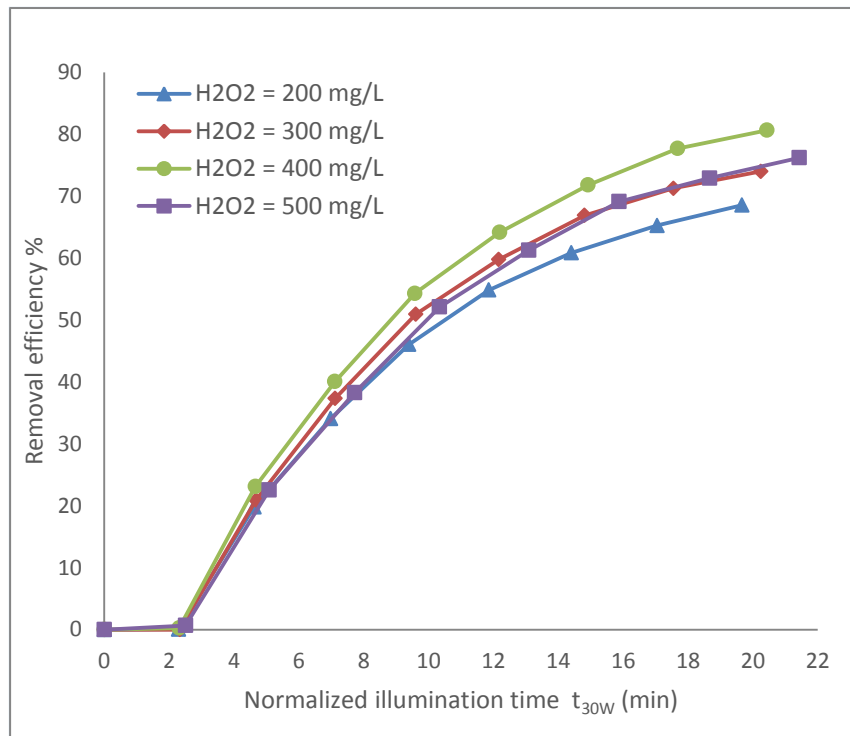
Figure6. Effect of initial H_2O_2 concentrations on the degradation of diuron by heterogeneous solar photocatalyst system at diuron conc.= 20 mg/L,TiO_2=400 mg/L.