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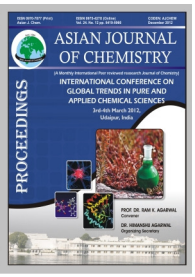

Sunlight Photocatalytic Degradation of Propanil in Aqueous Solution and Determination of Degraded Products with UV-and HPLC†

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The solar photocatalytic of an aqueous propanil were carried out under natural weathering conditions. Photocatalytic of 20 µg/mL propanil solution degraded 95 % of the solution after 3 h of solar irradiation, by using 10 mg of zinc oxide as a catalyst. The effect of various parameters such as amount of catalyst and illumination time on the degradation of propanil has been studied. The degradation percentages were investigated by monitoring the propanil mineralization spectrophotometrically. The mineralization rate of propanil is calculated.

Key Words: Sunlight, Degradation, Herbicide, Propanil, Determination.

INTRODUCTION

Water pollution is a serious problem faced throughout the world especially by chemical industries because of the toxic/hazardous. One of the compounds[1,2] involved, propanil is a very effective and therefore, widely used in an agriculture herbicide for inhibition of photosynthesis of weeds in rice crops[3] and other cultures (wheat, barley, oats, rye).

Propanil (3,4-dichloropropioanilide) is extensively used in Iraqi and other European countries for the control of some annual grasses and broadleaf weeds in several different crops, so the monitoring of propanil residues is very important to assess the safety of environment and food consequently, their residues have been detected in various natural waters in Iraq[4-6] and other European countries[7,8].

Crosby *et al.*[9] studied the photo degradation of propanil in aqueous medium under UV and sunlight irradiation. They found that propanil convert photochemically to 3,4-dichloroaniline and other aromatic compound solar photocatalysis aims at mineralizing the contaminants into carbon dioxide, water and inorganics[10,11]. In recent years interest has been focused on the use of semiconductor materials as photocatalysts for the removal of organic and inorganic species from aqueous or gas phase. This method has been suggested in environmental protection due to its ability to oxidize the organic and inorganic substrates[12-15].

The aim of this paper is to assess the effectiveness of the heterogeneous photocatalysis using ZnO under natural weathering condition for the decontamination of water polluted by propanil. This technique could utilize sunlight as a source of energy. Thus, the objectives of the study were (i) to evaluate the kinetics of disappearance of propanil and (ii) to identify the main intermediates in order to propose a photocatalytic degradation pathway.

EXPERIMENTAL

Propanil (3,4-dichloride propionanlide $C_9H_9NOCl_2$), herbicide supplied by sea Iraqi company(Stam F-34,360 g/L active ingredient) with purity of 98 %. The photocatalyst ZnO was purchased from E. Merck (99 %) purity. All other chemicals were used without further purification.

Propanil degradation was identified by UV-visible spectrophotometer (UV-visible 1650, spectrophotometer, Shimadzu, Japan and high performance liquid chromatographic (HPLC), Knauer, Germany). The determined wavelength was 248 nm, which is the maximum absorption wavelength.

Experiments were carried out in clear sunny days during august 2010. All experiments have been performed at Chemistry Department of Baghdad University, in an open atmosphere between 11.00 am -1.00 pm sunlight illumination was accomplished in a 250 mL conical flask containing 75 mL of the 20 µg/mL propanil solution.

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In all the experiments, 10 mg of the catalyst zinc oxide, was suspended using a magnetic stirrer in propanil solution, during the irradiation of the reaction mixture, 5 mL samples of the reaction mixture were, periodically, withdrawn using a syringe with a long pliable needle. These were centrifuged to separate the solid catalyst. In each case, 1 mL of the supernatant was drawn to measure the absorbance at 248 nm, using ultraviolet-visible spectrophotometer. To minimize the possible dark reactions, all samples were kept in the refrigerator in the dark.

The percentage of the initial propanil degraded per unit irradiation time was calculated by eqn. (1).

$$\text{Propanil degradation (\%)} = (C_0 - C_t)/ C_0 \times 100 \quad (1)$$

where C_0 is the initial concentration of propanil and C_t is the concentration of propanil at irradiation time. The absorption spectra of propanil is presented in Fig. 1.

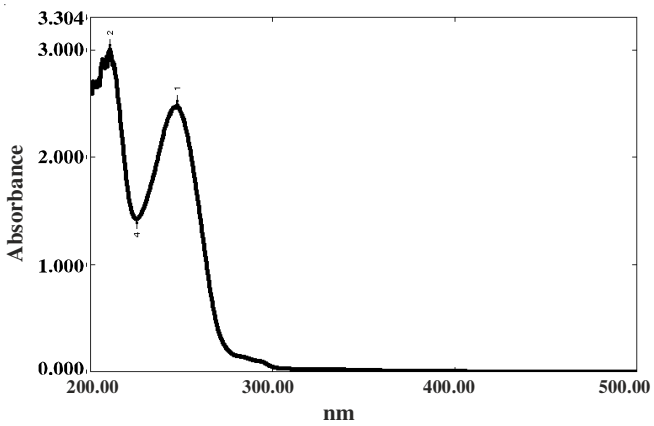


Fig. 1. Absorption spectra of propanil

RESULTS AND DISCUSSION

Effect of propanil concentration: The effect of concentration was studied at 10 to 100 µg/mL propanil levels in presence of 10 mg ZnO photocatalyst and 60 min of solar irradiation time. Initially, the photoremoval of propanil increased concomitantly with ZnO concentration due to more occupation of catalyst sites by the substrate and its subsequent photodecomposition. The photocatalytic removal of propanil under this experimental condition was highest at initial substrate concentration of 20 µg/mL (Fig. 2). As this concentration is exceeded, the photocatalytic removal of propanil decreased. Hence, 20 µg/mL was considered to be the optimum substrate concentration for this study.

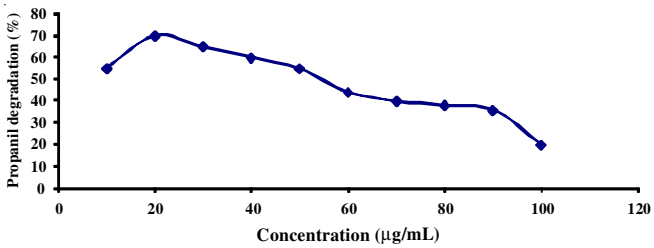


Fig. 2. Effect of initial concentration of propanil

Effect of catalyst mass: The effect of catalyst mass was investigated in the range of 1 to 15 mg at the 20 µg/mL initial propanil concentration and 1 h of solar irradiation time (Fig. 3). As seen from the figure, there is increase in propanil degradation between the photocatalyst concentration of 1 to 10 mg, which could be attributed to the increasing availability of photocatalyst sites. Above 10 mg ZnO concentration, the photocatalytic removal rate decreased due to light scattering by excess solid particles leading to poor light utilization. The optimum catalyst concentration (10 mg) obtained in this study.

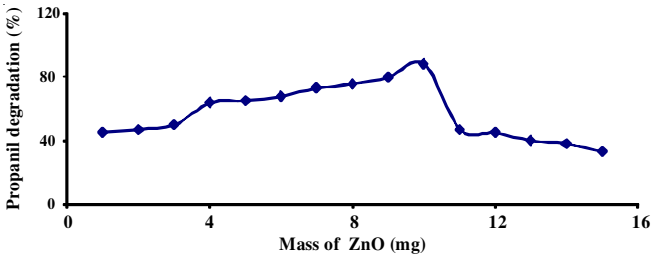


Fig. 3. Effect of mass of ZnO loading at 20 µg/mL initial propanil

Effect of illumination time: The effect of solar illumination time on the photocatalytic degradation of propanil in water with ZnO was investigated. The results are illustrated in Fig. 4. The photo-catalytic decomposition process proceeded rapidly until 60 min. At 180 min illumination time, propanil disappeared and degraded in aqueous solutions.

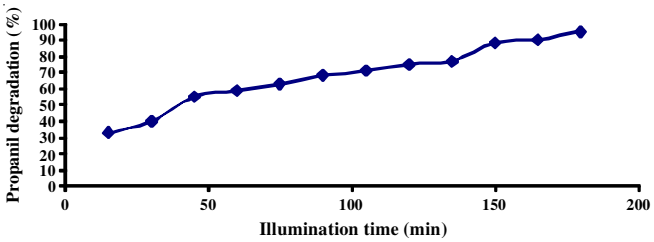
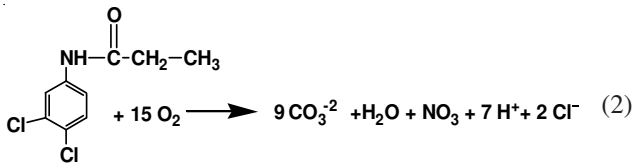


Fig. 4. Effect of solar illumination time on the solar photocatalytic degradation of propanil in aqueous solution using 10 mg ZnO.: and 20 µg/mL propanil

Kinetic degradation: The rate of photodegradation of propanil on ZnO catalyst was monitored under the optimum conditions employed for propanil (ZnO) loading is 10 mg and starting initial concentration 20 µg/mL in aqueous solution. We suggest the following mineralization by eqn. 2.



(2)

Graphical methods[16] were also employed to predict the order of reaction spectrophotometricaly. The degreases concentration of propanil in aqueous solution was monitored by the absorption at λ_{max} 248 nm with different irradiation time. The first order specific rate constant of the decomposition of propanil (k) was determined by the eqn. 3.

$$\text{Ln}(A_t - A_\infty) = \text{Ln}(A_0 - A_\infty) - k_t \quad (3)$$

where, A_t: the absorbance at time irradiation, A_∞: the absorbance for infinite time of irradiation, A_0: the absorbance before irradiation, k: specific the rate constant. Expressed in min^{-1}, t: time of solar irradiation.

The plot of the ln (A_t-A_∞) *versus* the sun irradiation time, shows a straight line behaviour. This suggests also the first-order kinetics of the photocatalst process. From the slope of straight line, the degradation of propanil and the value of the first order specific rate constant k_{phot} in aqueous solution, the value of the first order specific rate constant k is equal to 3.9×10^{-3} min^{-1} (Fig. 5).

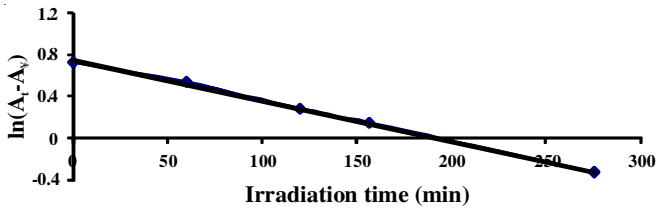


Fig. 5. Relation Between ln (A_t-A_∞) and the solar irradiation time for propanil in aqueous solution using 10 mg ZnO : and 20 µg/mL propanil

Identification of propanil photodegradation products: Ultraviolet-visible spectroscopy technique was used to monitor the formation of photodegradation products of propanil with ZnO suspension in aqueous solution. Fig. 6 show the absorption spectrum of propanil degradation in aqueous solution at different irreradation time in the spectral range between (200-500) nm.

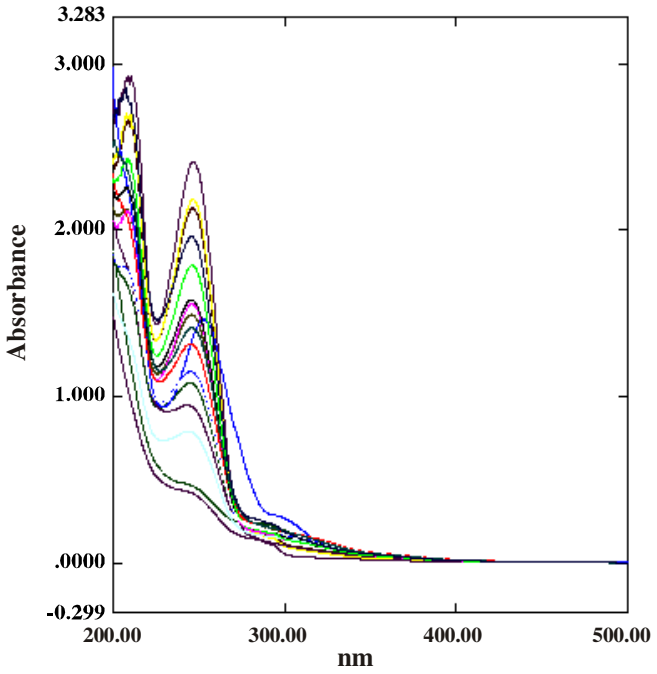


Fig. 6. UV-visible spectral change of degradation for solar photocatalytic degradation of propanil in aqueous solution using ZnO:10 mg, propanil : 20 µg/mL

The HPLC chromatogram showed the absorbance peak, which appeared at retention time of 7.8 min belong to propanil compound before sun radiation and after the irradiation the intensity of this peak is gradually decreased with irradiation time. A new absorbance peaks start to appear after 90 min irradiation time and this peaks located at 3.2 and 5.3 min. The test analysis of authentic compound reveals that these new peaks were related to propanoic acid and 3, 4-dichloro-aniline. After 120 min of irradiation the propanil peak continue to decrease and also the primary products peak starts to decrease. The complete decomposition showed after 180 min.

Photodegradation mechanism: A general ZnO photocatalytic mechanism is proposed[17,18] under the irradiation of energy greater than the band gap, valence band electrons are promoted to the conduction band leaving a hole behind eqn. 3. These electron (e^- cb)$^-$ hole (h^+_{vb}) pairs can either recombine eq. 4 or interact separately with other molecules. The holes at the ZnO valence band can oxidize adsorbed water or hydroxide ions to produce $^{\cdot}OH$ radicals (eqn. 5). Electron in the conduction band on the catalyst surface can reduce molecular oxygen to superoxide anion (eqn. 6).

This radical may form hydrogen peroxide or hydroperoxy radical $^{\cdot}OOH$ (eqns. 7 and 8). The hydroxyl radical is a powerful oxidizing agent and attacks to propanil and intermediate products are formed. These intermediates react with more hydroxyl radicals to produce final products CO_2 and H_2O (eqn. 9).

$$ZnO + h\nu \rightarrow ZnO\ (e^-_{cb}/h^+_{vb}) \rightarrow e^-_{cb} + h^+_{vb} \quad (3)$$

$$e^-_{cb} + h^+_{vb} \rightarrow \text{heat} \quad (4)$$

$$h^+_{vb} + OH^- \text{ (or } H_2O) \text{ ads} \rightarrow {}^{\cdot}OH\ (+ H^+) \quad (5)$$

$$e^-_{cb} + O_2 \rightarrow {}^{\cdot}O_2^- \quad (6)$$

$${}^{\cdot}O_2^- + H_2O + H^+ \rightarrow H_2O_2 + O_2 \quad (7)$$

$${}^{\cdot}O_2^- + H^+ \rightarrow {}^{\cdot}OOH \quad (8)$$

$$^{\cdot}OH \text{ (or } {}^{\cdot}OOH) + \text{propanil} \rightarrow \text{oxidative products} \rightarrow CO_2 + H_2O \quad (9)$$

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