Preparation and Investigation of Photocatalytic Properties of ZnO Nanocrystals: Effect of Operational Parameters and Kinetic Study

N. Daneshvar, S. Aber, M. S. Seyed Dorraji, A. R. Khataee, and M. H. Rasoulifard

Abstract—ZnO nanocrystals with mean diameter size 14 nm have been prepared by precipitation method, and examined as photocatalyst for the UV-induced degradation of insecticide diazinon as deputy of organic pollutant in aqueous solution. The effects of various parameters, such as illumination time, the amount of photocatalyst, initial pH values and initial concentration of insecticide on the photocatalytic degradation diazinon were investigated to find desired conditions. In this case, the desired parameters were also tested for the treatment of real water containing the insecticide. Photodegradation efficiency of diazinon was compared between commercial and prepared ZnO nanocrystals. The results indicated that UV/ZnO process applying prepared nanocrystalline ZnO offered electrical energy efficiency and quantum yield better than commercial ZnO. The present study, on the base of Langmuir-Hinshelwood mechanism, illustrated a pseudo first-order kinetic model with rate constant of surface reaction equal to 0.209 mg l^{-1} min^{-1} and adsorption equilibrium constant of 0.124 l mg^{-1}.

Keywords—Zinc oxide nanopowder, Electricity consumption, Quantum yield, Nanoparticles, Photodegradation, Kinetic model, Insecticide.

I. INTRODUCTION

THE presence of insecticide in the effluent of insecticide formulating and manufacturing industries severely affects the ecosystem. They are also used in different forms to overcome the loses from pests in the cultivation of plants. Though they contribute to a great extent in the agricultural productivity, they become major pollutant due to their extensive use. Diazinon (O-O-diethyle O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl] phosphorothioate) is an organophosphorous insecticide with widespread agricultural and non-agricultural uses, classified by the world Health Organization (WHO) as "moderately hazardous" class II. The primary environmental concerns associated with its use are bird kills, contamination of surface water and impacts on aquatic species [1].

The elimination of such toxic and hazardous chemicals from water and wastewater is presently one of the most important subjects in pollution control. Hence an effective is badly needed for treating such pollutants. Recently it has been demonstrated that semi-conducting materials mediated photocatalytic oxidation of organic compounds is a successful, convention alternative to conventional methods for the removal of organic pollutants from water. Till now, many kinds of semiconductors have been studied as photocatalyst including TiO_2, ZnO, CdS, WO_3 and so on. TiO_2 is the most widely used effective photocatalyst for its high efficiency, photochemical stability, non-toxic nature and low cost. As a contrast ZnO, a kind of semiconductor that has the similar band gap as TiO_2, is not thoroughly investigated. However, the greatest advantage of ZnO is that it absorb large fraction of solar spectrum and more light quanta than TiO_2 [2]. Some researches have highlighted the performance of ZnO on degradation some organic compounds [3, 4].

The purpose of this work was:

(1) To prepare ZnO nanocrystals and investigate their efficiency on the photocatalytic treatment of diazinon as a model compound.

(2) To study effects of process parameters in order to determination desired conditons.

(3) To calculate "electrical energy per order" and "quantum yield" for direct photolysis and photocatalysis.

(4) To investigate the efficiency of photocatalytic process in the real water containing diazinon.

(5) To study the kinetic of process based on Lanmuir-Hinshelwood model.

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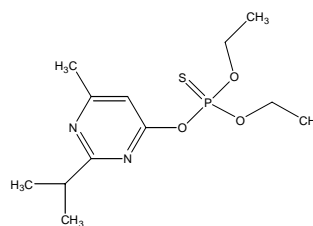
Fig. 1 Structure of diazinon

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II. EXPERIMENTAL

A. Materials

Diazinon, an insecticide, was obtained from Chem. Service (USA). The structure of diazinon has been depicted in Fig. 1. $ZnSO_4.7H_2O$, NaOH, H_2SO_4 and commercial ZnO powder are all analytical reagents and were obtained from Merck Co. (Germany).

B. Preparation of ZnO Nanocrystals

Nanocrystalline ZnO was prepared using the precipitation method. $ZnSO_4.7H_2O$ was used as the starting material and NaOH as precipitant without further purification. The resulting slurry was continuously stirred for 12 h, and then washed with deionized water. The wet powder was dried to form the precursor of ZnO. Finally, the precursor was calcined in air at a certain temperature to produce the nanosized ZnO photocatalyst. The average crystallite size (D in nm) of prepared ZnO nanopowder and commercial ZnO were determined from XRD patterns of the ZnO nanopowders (Fig. 2) according to the Debeye-Scherrer equation. The average particles sizes of commercial and prepared ZnO are about 33 and 14 nm, respectively. In all experiment, prepared ZnO nanoparticles with mean diameter, 14 nm were used.

C. Photoreactor and Procedure

All the experiments were carried out in a batch photoreactor. The radiation source was a UV lamp (30 W, UV-C, λ_{max} =253.7 nm, Philips), which placed above photoreactor. In the surface of solution the light intensity was 11.2 W/m^2 that was measured by CASSY Lab (Germany). The value of incident photon flux by reactor volume unit at 253.7 nm was 2.33×10^{-6} Einstein l^{-1} s^{-1}, which was calculated on the bases of the ferrioxalate actinometry measurments [5].

For the photodegradation of diazinon, a solution containing known concentration of the insecticide and ZnO nanopowder was prepared and it was allowed to equilibrate for 30 min in the darkness, then 50 ml of the prepared suspension was transferred to a 500 ml Pyrex reactor, then the lamp was switched on to initiate the reaction. During irradiation, the glass reactor mounted on a magnetic stirrer to keep the suspension homogenous and the suspension was sampled after an appropriate illumination time. Before determination of concentration of the insecticide, samples were filtered through disks to remove ZnO particles. The concentration of the insecticide in each degraded sample was determined using a spectrophotometer (UV/Vis Spectrophotometer, Perkin-Elmer 550 SE) at λ_{max} = 247 nm and a calibration curve. By this method conversion percent of diazinon can be obtained in different intervals. Then the degree of photodegradation (X) and remaining fraction (C/C$_o$) were calculated as functions of time.

D. Data Analysis

The quantum yield is a useful parameter in indicating the efficiency of a photodegradation reaction, and is defined as the number of molecules being decomposed per photon absorbed. The quantum yield of diazinon degradation can be calculated from the observed first-order degradation rate constant where a specific form of quantum yield, φ, based on first-order kinetics was indicated in Eq. 1:

$$\varphi = \frac{k}{2.303 I_{\circ,\lambda} \varepsilon_\lambda l} \qquad (1)$$

where $k(s^{-1})$ is the pseudo-first-order rate constant, φ is the quantum yield, $I_{\circ,\lambda}$ (Einstein l^{-1}s^{-1}) is the incident light intensity at wavelength λ, ε_λ (cm^{-1}M^{-1}) is the molar absorptivity at wavelength λ, and l is the cell path length (cm) [6].

The evaluation of the treatment costs is, at the moment, one of the aspects that need more attention. There are a number of important factors in selecting a waste treatment technology, including economics, economy of scale, regulations, effluent quality goals, operation (maintenance control, safety), and robustness (flexibility to change/upsets). Although all these factors are important, economics is often paramount. Since the UV/ZnO process is electric energy intensive process, and electric energy can represent a major fraction of the operating costs, simple figures-of-merit based on electric energy consumption can be very useful and informative. In the case of low pollutant concentration (which applies here), the appropriate figure-of-merit is the electrical energy per order (E_{EO}), defined as the number of kilowatt hours of electrical energy required to reduce the concentration of a pollutant by 1 order of magnitude in a unit volume of contaminated water. The E_{EO} (kWh/m^3/order) can be calculated from the following equations for a batch type reactor:

$$E_{EO} = \frac{P \times t \times 1000}{V \times 60 \times \log(C_o / C)} \qquad (2)$$

where P is the input power (kW) to the AOP system, t is the irradiation time (min), V is the volume of water (l) in the reactor, C_o and C are the initial and final pollutant concentrations, respectively [7].
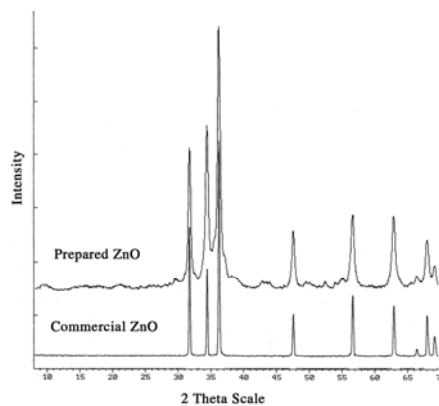

Fig. 2 XRD patterns of prepared and commercial ZnO nanocrystals

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III. RESULTS AND DISCUSSION

### A. Effect of ZnO Nanocrystals and UV Irradiation

The change in the insecticide concentration vs. time profile during the photocatalytic degradation of diazinon is shown in Fig. 3. The photodegradation of diazinon was negligible in the absence of nanocrystalline ZnO powder. Removal of diazinon was less than 8% in the direct photolysis indicating that the observed high decomposition in the UV/ZnO process is exclusively attributed to the photocatalytic reaction of the semiconductor particles.

B. Effect of ZnO Dosage

For economic removal of insecticide effluent from wastewater, it is necessary to find the optimum amount of catalyst for efficient degradation. The relationship between the photodegradation efficiency of diazinon and concentration of nanophotocatalyst is shown in Fig. 4. From Fig. 4, it can be seen that when the illumination time is fixed, as the concentration of thephotocatalyst increases from 25 to 150 mg l^{-1}, the degree of photodegradation of diazinon increases from 0.39 to 0.65. Further increases of catalyst concentration beyond 150 mgl^{-1} do not affect the degradation significantly. This observation can be explained in terms of availability of active sites on the catalyst surface and the penetration of UV light into the suspension. [8].

C. Effect of pH

The solution pH is an important variable in the evaluation of aqueous phase mediated photocatalytic reactions. The effect of pH on remaining fraction was studied by keeping all other experimental conditions constant and changing the initial pH value of the insecticide solution from 3.5 to 11 and results are illustrated in Fig. 5. The remaining fraction of diazinon decreases with increase in pH from 3.5 to 5.2 and then increases. Since the pHzpc of ZnO is 9.0, the surface of the catalyst is positive below pH 9.0. Again the given pKa for diazinon is 2.6, therefore diazinon is negatively charged above pH 2.6 that might result in electrostatic attraction between the nanocatalyst and diazinon and will increase both adsorption and the degree of photodegradation. Unfortunately, the mere electrostatic argument is unable to exhaustively account for the relative photocatalytic behaviour as a function of pH. Other concomitant effect can come into play. For example ZnO can undergo photocorrosion through self-oxidation (Eq. 3). In particular, ZnO powder exhibit tendency to dissolve with decreasing the pH (Eq. 4).

$$ZnO + 2h^+ \rightarrow Zn^{2+} + \frac{1}{2}O_2 \qquad (3)$$

$$ZnO + 2H^+ \rightarrow Zn^{2+} + H_2O \qquad (4)$$
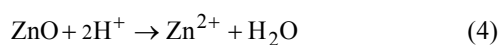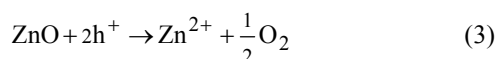
In a strongly alkaline environment, ZnO can undergo dissolution according to [9]:

$$ZnO + H_2O + 2OH^- \rightarrow Zn(OH)_4^{2-} \qquad (5)$$
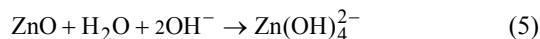
Therefore, reduce of photocatalytic activity of ZnO at exceedingly low and high pH values can originate from either acidic/photochemical corrosion of the catalyst (Eqs. 3, 4), from alkaline dissolution (Eq. 5). In addition reactions 3 and 5 can compete with the formation of hydroxyl radicals by decreasing the availability of holes for water or surface OH$^-$ oxidation.

D. Effect of Initial Diazinon Concentration

The effect of various initial insecticide concentrations on the photocatalytic degradation of diazinon has been investigated from 16 to 30 mg l^{-1}. The results are shown in Fig. 6. Increase in the concentration of insecticide from 16 to 30 mg l^{-1} increases the remaining fraction from 0.27 to 0.63, in 50 min of UV irradiation. This may be due to the fact that with the increase in initial concentration of diazinon, while the UV light irradiation period and catalyst dose are kept constant, more insecticide molecules are adsorbed onto the surface of ZnO.
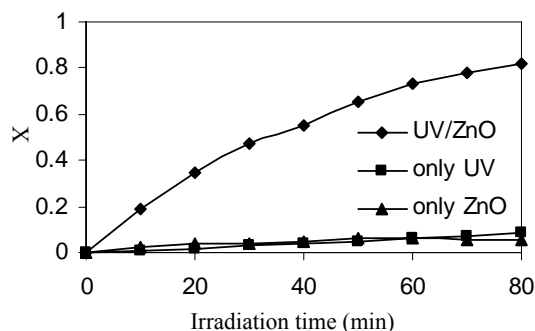

Fig. 3 Effect of ZnO nanoparticles and UV light on photocatalytic degradation of diazinon

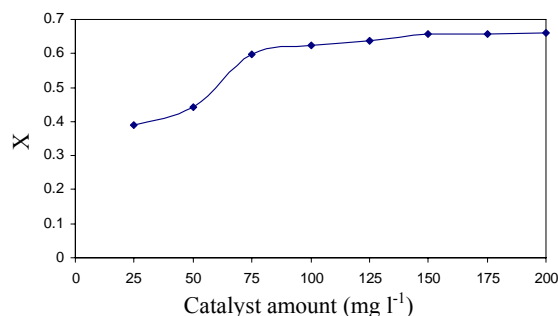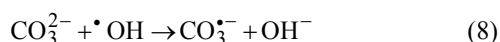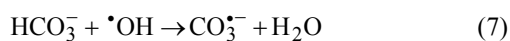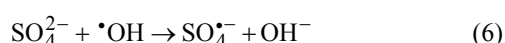[diazinon] $_\circ$ = 20 mgl^{-1}; [ZnO]= 150 mgl^{-1}; pH neutral

Fig. 4 Effect of catalyst loading on the degree of photodegradation diazinon. [diazinon] $_\circ$ = 20 mgl^{-1}; pH neutral; irradiation time = 50min

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E. Treatment of Real Water Containing Diazinon

In order to investigate the efficiency of UV/ZnO process in removal of diazinon from real water, 20 ppm of insecticide was added into a real water sample (Carbonate hardness: 88 mgl^{-1} $CaCO_3$, Sulphate concentration: 172.8 mgl^{-1} SO_4^{2-}) that was obtained from irrigation well in Tabriz, Iran.

The effect of presence of common anions such as sulphate, carbonate and bicarbonate on the photocatalytic degradation of diazinon is shown in Fig. 7. It is clear from this figure that, in presence of SO_4^{2-}, HCO_3^- and CO_3^{2-} the percent of degradation decreases. This inhibition is undoubtedly due to their ability to act as hydroxyl radical's scavengers by the following reaction [10]:

$$SO_4^{2-} + {}^\bullet OH \rightarrow SO_4^{\bullet -} + OH^- \qquad (6)$$

$$HCO_3^- + {}^\bullet OH \rightarrow CO_3^{\bullet -} + H_2O \qquad (7)$$

$$CO_3^{2-} + {}^\bullet OH \rightarrow CO_3^{\bullet -} + OH^- \qquad (8)$$

These ions may also block the active sites on the ZnO surface thus deactivating the catalysts towards the diazinon and intermediate molecules. Although, the generated radical anions have been shown to be an oxidant itself, but its oxidation potential is less than that of the hydroxyl radicals. The increase of remaining fraction in real water might also be attributed to increase of pH in real water because of presence of carbonate and bicarbonate ions in compared with distilled water.

F. Comparison of Photocatalytic Activity of Prepared and Commercial ZnO Nanocrystals

Fig. 8 shows the photodegradation results of diazinon with prepared and commercial ZnO. The results of Fig. 8 gave us the intuitional impression about the effect of size on the degradation efficiency for two different ZnO catalysts.The effect of size on the photodegradation efficiency can be ascribed to following reasons: when the size of ZnO crystals decreases, the amount of the dispersion particles per volume in the solution will increase, resulting the enhancement of the photon absorbance, at the same time, the surface area of ZnO photocatalyst will increase, which will promote the adsorption of more insecticide molecules on the surface.

G. Kinetics of Photocatalytic Degradation of Diazinon

The photocatalytic degradation of diazinon with ZnO obeys apparently pseudo-first order kinetics at low initial insecticide concentration and the rate expression is given by Eq. (9).

$$\ln[\frac{C_\circ}{C}] = kt \qquad (9)$$

where k is the pseudo-first order rate constant, C and $C_\circ$ are the concentration at time 't' and 't=0', respectively.

Table I reports the values of k resulting from plot of

$\ln(C_\circ/C)$ versus 't' for photocatalytic degradation of diazinon, which decreases as the initial reactant concentration increases. This can be ascribed to the decrease in the number of active sites on the catalyst surface due to the covering of the surface with diazinon molecules, which is directly proportional with the initial concentration of diazinon. Many authors [11, 12] have used the modified Langmuir-Hinshelwood (L-H) kinetic expression to analyze the heterogeneous photocatalytic reaction successfully. The experimental data has been rationalized in terms of the modified form of L-H kinetic model to describe the solid-liquid reaction successfully. The rate of oxidation of insecticide at surface reaction is proportional to the surface coverage of diazinon on the ZnO assuming that the insecticide is strongly adsorbed on the catalyst surface than the intermediate products. The effect of initial concentration of organic substrate on the initial degradation rate (r) is given in the form of Eq. (10) and (11).

$$r = \frac{K_{diazinon} k_c [C]}{1 + K_{diazinon} [C]_\circ} = k[C] \qquad (10)$$

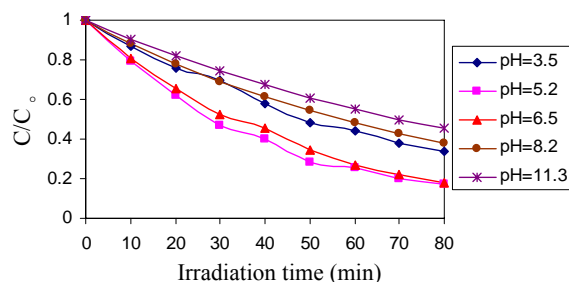$$\frac{1}{k} = \frac{1}{K_{diazinon} k_c} + \frac{[C]_\circ}{k_c} \qquad (11)$$

Fig. 5 Effect of pH on photocatalytic degradation of diazinon
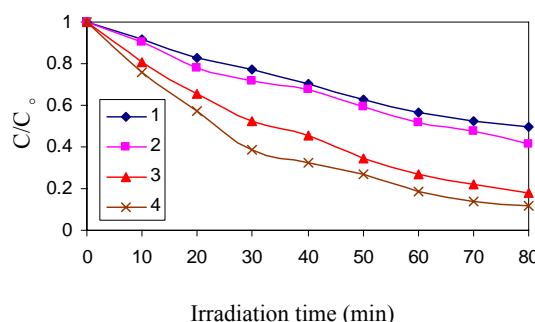[diazinon] $_\circ$ = 20 mgl^{-1}; [ZnO]= 150 mgl^{-1}

Fig. 6 Effect of initial insecticide concentrations on the degradation of diazinon. [ZnO]= 150 mgl^{-1}; pH neutral; [1] =30 mgl^{-1}; [2]= 25 mgl^{-1}; [3]=20mgl^{-1}; [4]=16 mgl^{-1}

where $K_{diazinon}$ and k_c are the Langmuir-Hinshelwood adsorption equilibrium constant and rate constant of surface

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reaction, respectively. At low concentrations, i.e., concentrations up to 40 mg l^{-1}, the applicability of L-H equation for the photocatalytic degradation has been confirmed by the linear plot obtained by plotting reciprocal of rate constant (1/k) against initial concentration ([C] $_o$) as shown in Fig. 9. The values $K_{diazinon}$ and k_c are found to be 0.124 mg^{-1}l and 0.209 mg l^{-1} min^{-1}, respectively.

H. Electrical Energy Efficiency

The E_{EO} values for degradation of diazinon by photolysis, UV/ZnO (33nm) and UV/ZnO (14nm) processes were 20000, 1388.8 and 1075.3 kWh/m^3, respectively. The E_{EO} values showed that electrical efficiency in the photocatalysis process is better than in photolysis system. It is also clear that the photocatalysis process in presence of ZnO with mean size 14 nm offered the best energy efficiency.

I. Determination of the Quantum Yield

The quantum yield values for photodegradation of diazinon by photolysis, UV/ZnO (33nm) and UV/ZnO (14nm) processes under the illumination of UV at 253.7 nm were 0.0007, 0.01 and 0.013, respectively. The results indicated that in the presence of ZnO, the photocatalysis quantum yield obtained higher than direct photolysis quantum yield, suggesting that photodecay of diazinon was dominated by photocatalysis.

TABLE I
DIAZINON CONVERSION (AT 50 MIN) AND PSEUDO-FIRST-ORDER KINETIC RATE CONSTANT IN PHOTOCATALYTIC EXPERIMENTS WITH DIFFERENT INITIAL CONCENTRATION

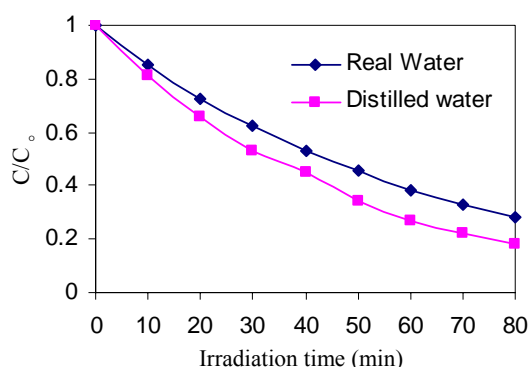| [diazinon] $_o$ (mgl^{-1})	X_5	k	r^2
16	0.86	0.027	0.98
20	0.66	0.0215	0.99
25	0.41	0.0107	0.99
30	0.37	0.0091	0.99
40	0.27	0.0068	0.99

Fig. 7 Investigation the efficiency of UV/ZnO process in removal of diazinon from real water.
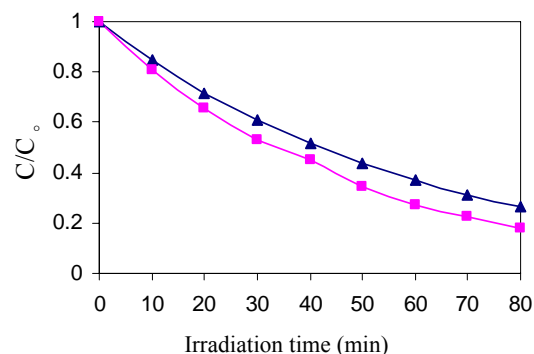
[diazinon] $_o$ =20 mgl^{-1}; [ZnO] $_o$ =150 mgl^{-1}

Fig. 8 Comparison of photodegradation efficiency of diazinon in the presence of prepared and commercial ZnO nanocrystals [diazinon] $_o$ =20 mgl^{-1}; [ZnO] $_o$ =150 mgl^{-1};pH neutral.
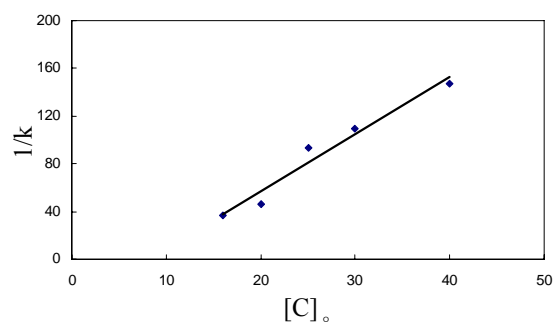▲ commercial ZnO (33nm) ■ prepared ZnO (14nm)

Fig. 9 Determination of the adsorption equilibrium constant, $K_{diazinon}$ and the kinetic rate constant of surface, k_c for the Langmuir-Hinshelwood

IV. CONCLUSION

The photodegradation of diazinon in this study has reached several conclusive statements:

(1) Photocatalytic degradation of diazinon was negligible when ZnO nanopowder and UV light were used on their own.

(2) The results indicated that degree of degradation of diazinon was obviously affected by illumination time, pH and photocatalyst loading. (3) The electrical energy consumption per order of magnitude for photocatalytic degradation of diazinon was lowest in the UV/ZnO (prepared) process than that in the UV and UV/ZnO (commercial) processes. (4) The results indicaed that the photocatalysis process in the presence of ZnO with mean size 14 nm offered the highest quantum yield. (5) The kinetics of photocatalytic removal of diazinon followed the Langmuir-Hinshelwood model.

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