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

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Photocatalytic degradation of the insecticide diazinon in the presence of prepared nanocrystalline ZnO powders under irradiation of UV-C light

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Abstract

ZnO nanocrystals were prepared by precipitation method. After aging, washing and drying, solids were calcined at 300 °C and examined as photocatalyst for UV-induced degradation of organophosphorus insecticide diazinon in aqueous solution. The average crystallite size of prepared ZnO nanopowder was determined from XRD pattern using Debeye–Scherrer equation in the range of 14 nm. The experiment showed that ZnO nanopowder and UV light had a negligible effect when they were used on their own. The effects of some operational parameters such as pH value, nanocatalyst loading and initial insecticide concentration on the degradation efficiency were discussed through the photocatalytic experiments using prepared ZnO nanocrystals as the photocatalyst. In this case the optimized parameters were also tested for the treatment of real water containing the insecticide. A model was successfully established for the prediction of degradation of diazinon in UV/ZnO process with any concentration of insecticide. Catalytic activities of prepared and commercial ZnO nanocrystals were also compared. The diazinon photodegradation quantum yield in UV/ZnO process increased with decreasing the diameter size of ZnO from 33 to 14 nm. The results showed that the photocatalysis process in the presence of ZnO with mean size of 14 nm offered the best energy efficiency. Accordingly, it could be stated that 80% removal of the insecticide, after selecting desired operational parameters could be achieved in a relatively short time, about 80 min.
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Keywords: Zinc oxide; Nanocrystal; Diazinon; Quantum yield; Kinetic model

1. Introduction

Presently, a wide variety of pesticides are introduced into the water system from various sources, such as industrial effluent, agricultural runoff and chemical spills. Their toxicity, stability to natural decomposition and persistence in the environment has been the cause of much concern to societies and regulation authorities around the world [1].

Diazinon a phosphorothioate commercially introduced in 1952 is used as an insecticide for different types of cultivation such as fruit trees, rice, sugarcane, corn, tobacco and horticultural plants because of its inhibition of the acetylcholinesterase

of most kinds of insects [2]. Diazinon (*O*,*O*-diethyl *O*-[2-isopropyl-6-methylpyrimidin-4-yl] thiophosphate) is classified by the World Health Organization (WHO) as "moderately hazardous" class II. It was associated with toxicity to aquatic organisms at concentration of $350\,ng\,l^{-1}$ [3], with an LC_{50} in killifish (48 h) of $4.4\,mg\,l^{-1}$ [2]. Fatal human doses were found to be in the range from 90 to $444\,mg\,kg^{-1}$ [3]. Toxic effects of diazinon are attributed to its inhibition of the enzyme acetylcholinesterase [4]. Diazinon is relatively water soluble, moderately mobile and persistent in soil, hence, it is of concern for groundwater and surface derived drinking water. Diazinon has a vapour pressure of 1.4×10^{-4} mm Hg at 20 °C and Henry's law constant of 1.4×10^{-6} atm m^3 mol^{-1}, which would indicate that it would not easily volatilize from water and soil [5].

In recent years, as a promising tool to substitute the traditional wastewater treatment, semiconductor-assisted photocatalysis among the advanced oxidation processes (AOPs) has attracted the public concern for its ability to convert the pollutants into the harmless substances directly in the wastewater. Till now, many kinds of semiconductor have been studied as photocata-

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lysts including TiO_2, ZnO, CdS, WO_3 and so on [6–8]. 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 biggest advantage of ZnO in comparison with TiO_2 is that it absorbs over a larger fraction of UV spectrum and the corresponding threshold of ZnO is 425 nm [9]. Some researches have highlighted the performance of ZnO on degradation of some organic compounds. ZnO nanopowder has been reported, sometimes, to be more efficient than TiO_2 and its efficiency has been pointed out to be particularly noticeable in the advanced oxidation of pulp mill bleaching wastewater [10,11], the photooxidation of 2-phenylphenol and photocatalysed oxidation of phenol [12].

Kouloumbos et al. [4] identified the formation of several intermediates in degradation of diazinon with UV/TiO_2 process using GC/ion-trap mass spectrometry. They reported diazoxon, hydroxydiazinon and 2-isopropyl-6-pyrimidinol (IMP) as oxidation intermediate of diazinon photocatalytic degradation process.

The aim of present work is to study the photocatalytic activity of prepared ZnO nanocrystals. For this purpose, the nano-sized ZnO was prepared by precipitation method and examined as photocatalyst for UV-induced photocatalytic degradation (UV/ZnO process) of diazinon as a model of organic compounds. The effect of UV light irradiation, pH, catalyst loading and the initial concentration of pollutant was examined on photodegradation efficiency. The efficiency of photocatalytic process was investigated in the real water containing diazinon. The E_{EO} "Electrical energy per order" and quantum yields for both direct photolysis and photocatalysis were calculated. Prepared and commercial ZnO powder were also compared for the photodecay of diazinon aqueous solution. According to kinetic studies a model was successfully established for the prediction of degradation of diazinon in UV/ZnO process with any concentration of insecticide.

2. Experimental

2.1. Materials

Diazinon, an insecticide was purchased from Chem-service (USA) and used as received. Its chemical structure and other characteristics are listed in Table 1. $ZnSO_4 \cdot 7H_2O$, NaOH, H_2SO_4 and commercial ZnO powder are all analytical reagents and were obtained from Merck Co. (Germany).

2.2. Preparation of nanocrystalline ZnO

Nanometer oxide ZnO was prepared using the precipitation method. $ZnSO_4 \cdot 7H_2O$ was used as the starting material and NaOH as precipitant without further purification. NaOH solution was added dropwise to the vigorously stirred solution to adjust pH to about 7 and a large amount of white slurry was formed. The resulting slurry was continuously stirred for 12 h, and then washed with deionized water. The wet powder was dried at about

Table 1
Structure and characteristics of diazinon
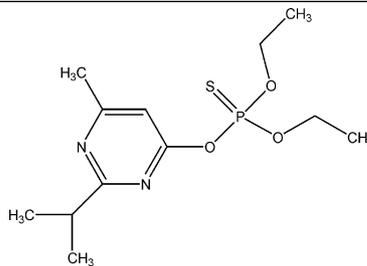
Structure	
λ_{max} (nm)	247
M_w (g mol^{-1})	304.3
Density (g ml^{-1}) (20 °C)	1.11
WHO class	II

100 °C in air to form the precursor of ZnO. Finally, the precursor was calcined in air at a certain temperature (300 °C for 3 h) to produce the nano-sized ZnO photocatalyst.

X-ray diffraction (XRD) patterns were carried out on a Simens D-5000 diffractometer with Cu Kα adiation (Germany). The average crystallite size (D in nm) of prepared ZnO nanopowder and commercial ZnO were determined from XRD patterns of the ZnO nanopowders (Fig. 1) according to the Debeye–Scherrer equation: $D = k(\lambda/(\beta \cos \theta))$ where k is a constant equal to 0.89, λ the X-ray wavelength equal to 0.154056 nm, β the full width at half maximum and θ is the half diffraction angle (17.61) [13]. The average particles sizes of commercial and prepared ZnO are about 33 and 14 nm, respectively. The XRD patterns in Fig. 1 show clearly different intensity ratio of reflection (0 0 2) and (1 0 0) for prepared ZnO when compared to the commercial ZnO. This comparison show I(0 0 2)/I(1 0 0) ratio <1 for commercial ZnO and I(0 0 2)/I(1 0 0) ratio >1 for prepared ZnO. This clearly
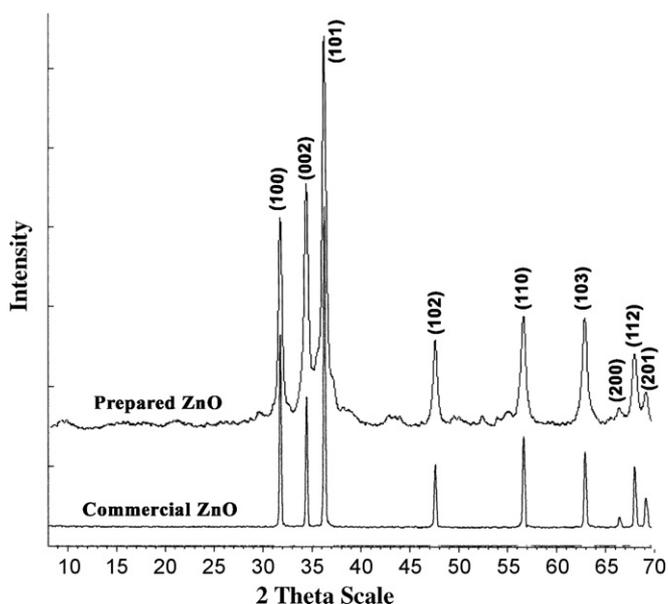

Fig. 1. XRD pattern of ZnO nanocrystals prepared by precipitation method and commercial ZnO.

shows that the prepared and commercial ZnO nanocatalysts are morphologically difference [14]. To determine the specific surface area of the prepared and commercial ZnO, gas sorption analysis (Brunauer–Emmett–Teller (BET) method) was carried out by using a Quantachrome ChemBET (USA). Results indicate the specific surface area of prepared and commercial ZnO are 16 and 10 $m^2 g^{-1}$, respectively. In all experiments, prepared ZnO nanoparticles with mean diameter, 14 nm were used.

2.3. Procedure

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. Irradiation was carried out with a 30 W (UV-C) mercury lamp (Philips, Holland), which was put above the batch photoreactor. The distance between solution and UV source was constant, 15 cm, in all experiments. 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 measurements [15]. The suspension pH values were adjusted at desired level using dilute NaOH and H_2SO_4 and then the pH values were measured with pH meter (Philips PW 9422, Holland). After that, the lamp was switched on to initiate the reaction. During irradiation, agitation was maintained by a magnetic stirrer (Ogawa Seiki, Japan) to keep the suspension homogeneous, 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, USA) at $\lambda_{max} = 247$ nm and a calibration curve. By this method conversion percent of diazinon can be obtained in different intervals. The degree of photodegradation (X) as a function of time is given by

$$X = \frac{C_0 - C}{C_0} \tag{1}$$

where C_0 is the initial concentration of diazinon, and C is the concentration of diazinon at time t.

3. Results and discussion

3.1. Efficiency of photocatalyst

The change in the insecticide concentration versus time profile during the photocatalytic degradation of diazinon is shown in Fig. 2. 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. It can be seen from the figure that in the
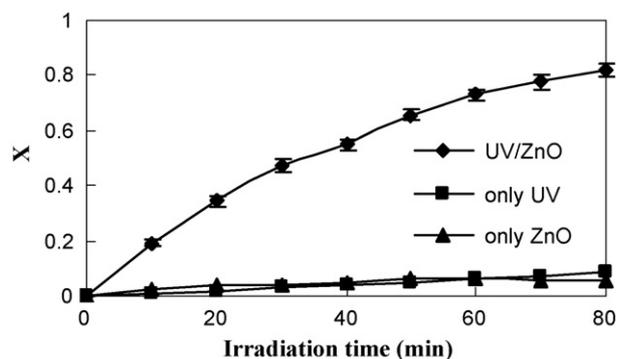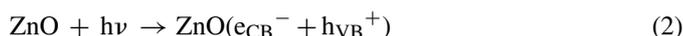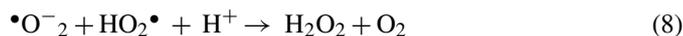

Fig. 2. Effect of UV light and ZnO nanoparticles on photocatalytic degradation of diazinon. $[diazinon]_0 = 20 \, mg \, l^{-1}$; $[ZnO] = 150 \, mg \, l^{-1}$; pH neutral.

presence of both ZnO nanopowder and UV light, 80% removal of the insecticide could be achived in short time, about 80 min. These experiments demonstrated that both UV light and a photocatalyst, such as ZnO were needed for the effective destruction of diazinon. Because it has been established that the photocatalytic degradation of organic matter in solution is initiated by photoexcitation of the semiconductor, followed by the formation of an electron–hole pair on the surface of catalyst (Eq. (2)). The high oxidative potential of the hole ($h_{VB}{}^+$) in the catalyst permits the direct oxidation of organic matter (insecticide) to reactive intermediates (Eq. (3)). Very reactive hydroxyl radicals can also be formed either by the decomposition of water (Eq. (4)) or by the reaction of the hole with OH^- (Eq. (5)). The hydroxyl radical is an extremely strong, non-selective oxidant that leads to degradation of organic chemicals [9,12,16]:

$$ZnO + h\nu \rightarrow ZnO(e_{CB}{}^- + h_{VB}{}^+) \tag{2}$$

$$h_{VB}{}^+ + \text{insecticide} \rightarrow \text{oxidation of the insecticide} \tag{3}$$

$$h_{VB}{}^+ + H_2O \rightarrow H^+ + {}^\bullet OH \tag{4}$$

$$h_{VB}{}^+ + OH^- \rightarrow {}^\bullet OH \tag{5}$$

Electron in the conduction band ($e_{CB}{}^-$) on the catalyst surface can reduce molecular oxygen to superoxide anion (Eq. (6)). This radical, in the presence of organic scavengers, may form organic peroxides (Eq. (7)) or hydrogen peroxide (Eq. (8)):

$$e_{CB}{}^- + O_2 \rightarrow {}^\bullet O^-{}_2 \tag{6}$$

$${}^\bullet O^-{}_2 + \text{insecticide} \rightarrow \text{insecticide} - OO^\bullet \tag{7}$$

$${}^\bullet O^-{}_2 + HO_2{}^\bullet + H^+ \rightarrow H_2O_2 + O_2 \tag{8}$$

Electrons in the conduction band are also responsible for the production of hydroxyl radicals, which have been indicated as the primary cause of organic matter mineralization (Eq. (9)) [16,17]:

$${}^\bullet OH + \text{insecticide} \rightarrow \text{degradation of the insecticide} \tag{9}$$

3.2. Effect of catalyst loading

The effect of catalyst loading on degradation of diazinon was investigated using ZnO from 25 to $200 \, mg \, l^{-1}$ keeping another parameters constant. The results are shown in
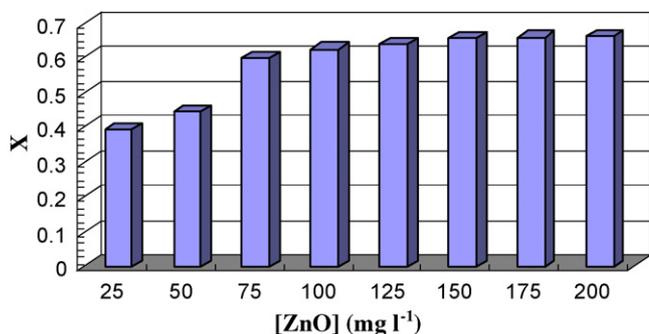
Fig. 3. Effect of ZnO amount on photodegradation efficiency of diazinon at irradiation time of 50 min. $[diazinon]_0 = 20\,mg\,l^{-1}$; pH neutral.

Fig. 3. Experiments performed with different concentrations of ZnO nanopowder showed that the photodegradation efficiency increased with an increase in ZnO nanopowder concentration up to 150 ppm, and after that the increase in catalyst loading dose 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. The total active surface area increases with increasing catalyst dosage. At the same time, due to an increase in the turbidity of the suspension, there is a decrease in UV light penetration as a result of increased scattering effect and hence the photoactivated volume of suspension decreases. Further, at high catalyst loading, it is difficult to maintain the suspension homogenous due to particles agglomeration, which decreases the number of active sites [9,16,18,19]. Since the most effective decomposition of diazinon was observed with 150 ppm of ZnO nanopowder, the other experiments were performed in this concentration of ZnO nanopowder.

3.3. Effect of initial diazinon concentration

The influence of initial concentration of diazinon solution on the photocatalytic degradation is an important aspect of the study. The effect of this parameter on the degree of photodegradation was studied by varying the initial concentration over a range of $16–30\,mg\,l^{-1}$. The results are illustrated in Fig. 4. The degree of photodegradation decreased with increasing of initial concentration of insecticide. When initial concentration increase, more organic substances are adsorbed on the surface of ZnO. Therefore, there are only a fewer active sites for adsorption
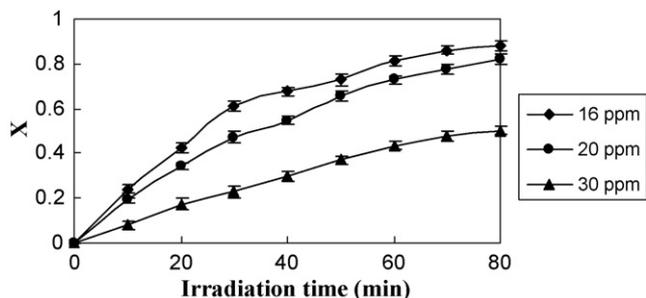

Fig. 4. Effect of initial insecticide concentration on photocatalytic degradation efficiency of diazinon. [ZnO] = 150 ppm; pH neutral.
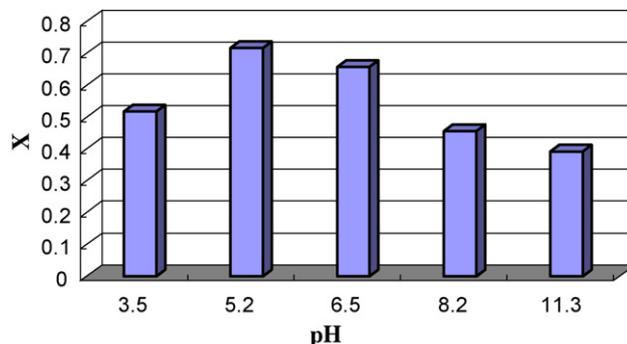

Fig. 5. Effect of pH on photocatalytic degradation of diazinon at irradiation time of 50 min. $[diazinon]_0 = 20\,mg\,l^{-1}$; $[ZnO] = 150\,mg\,l^{-1}$.

of hydroxyl ions so the generation of hydroxyl radicals will be reduced. Further, as the concentration of an insecticide solution increase, the photons get intercepted before they can reach the catalyst surface, hence the adsorption of photons by the catalyst decreases, and consequently the degradation percent is reduced [20–22].

3.4. Effect of pH values

pH can be one of the most important parameters for the photocatalytic process and so it was of interest to study its influence on the photocatalytic degradation of diazinon. In Fig. 5 the degree of photodegradation of diazinon at a fixed reaction time (50 min) is reported in the pH range of 3.5–11.3. The results indicated that the degree of photodegradation increased with increasing pH up to 5.2 and then decreased. Generally, the effect of pH on organic degradation assisted by the semiconductor oxides has been related to the establishment of acid–base equilibria governing the surface chemistry of metal oxides in water [23–26]:

$$ZnOH_2^{+} \Leftrightarrow ZnOH + H^{+} \quad pK_{a_1} \tag{10}$$

$$ZnOH + OH^{-} \Leftrightarrow ZnO^{-} + H_2O \quad pK_{a_2} \tag{11}$$

The pH at which the surface of an oxide is uncharged is defined as the zero point charge (pH_{ZPC}). It has been reported that the pH of zero point charge for ZnO is 9.0 [27]. The given pK_a for diazinon is 2.6. The effect of pH on the photocatalytic performance can be thus explained in terms of electrostatic interaction between the catalyst surface and the target substrate. Such interaction can be expected to affect the encounter probability of the nascent hydroxyl radical with the insecticide. It follows that the overall reaction would be enhanced or hindered depending on whether attractive or repulsive forces prevail, respectively. Diazinon is negatively charged above pH 2.6, whereas catalysts are positively charged below pH $\cong 9$. As expected, optimal conditions were found at $pK_a^{diazinon} < pH < pH_{ZPC}^{ZnO}$ at which the positively charged ZnO and negatively charged insecticide molecules should readily attract each other. 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. (12)) [23,28]:

$$ZnO + 2h^+ \rightarrow Zn^{2+} + \frac{1}{2}O_2 \tag{12}$$

In particular, ZnO powder exhibit tendency to dissolve with decreasing the pH (Eq. (13)) [16]:

$$ZnO + 2H^+ \rightarrow Zn^{2+} + H_2O \tag{13}$$

In a strongly alkaline environment, ZnO can undergo dissolution according to

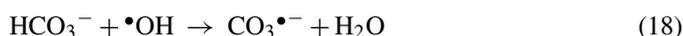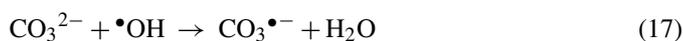$$ZnO + H_2O + 2OH^- \rightarrow Zn(OH)_4{}^{2-} \tag{14}$$

Moreover, the possible formation of photocatalytically inert Zn(OH)$_2$ surface layers upon UV irradiation (Eq. (15)) has also to be considered in aqueous media [29]:

$$2ZnO + 4H_2O + 4h^+ \rightarrow 2Zn(OH)_2 + O_2 + 4H^+ \tag{15}$$
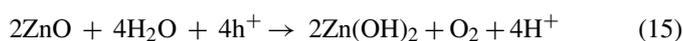
Therefore, the reduction of photocatalytic activity of ZnO at exceedingly low and high pH values can originate from either acidic/photochemical corrosion of the catalyst (Eqs. (12) and (13)), from alkaline dissolution (Eq. (14)) and/or surface passivation with Zn(OH)$_2$ (Eq. (15)). In addition reactions (12) and (14) can compete with the formation of hydroxyl radicals by decreasing the availability of holes for water or surface OH$^-$ oxidation.

3.5. Treatment of a 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 that was obtained from irrigation well in Tabriz, Iran. The characteristics of the real water are presented in the Table 2. The effect of presence of common anions such as sulphate, carbonate and bicarbonate on the photocatalytic degradation of diazinon is shown in Fig. 6. It is clear from this figure that, in presence of SO$_4{}^{2-}$, HCO$_3{}^-$ and CO$_3{}^{2-}$ the degradation percent decreases. This inhibition is undoubtedly due to their ability to act as hydroxyl radical's scavengers by the following reaction [30,31]:

$$SO_4{}^{2-} + {}^\bullet OH \rightarrow SO_4{}^{\bullet -} + OH^- \tag{16}$$

$$CO_3{}^{2-} + {}^\bullet OH \rightarrow CO_3{}^{\bullet -} + H_2O \tag{17}$$

$$HCO_3{}^- + {}^\bullet OH \rightarrow CO_3{}^{\bullet -} + H_2O \tag{18}$$

These ions may also block the active sites on the ZnO surface thus deactivating the catalysts towards the diazinon and

Table 2
Characteristics of real water

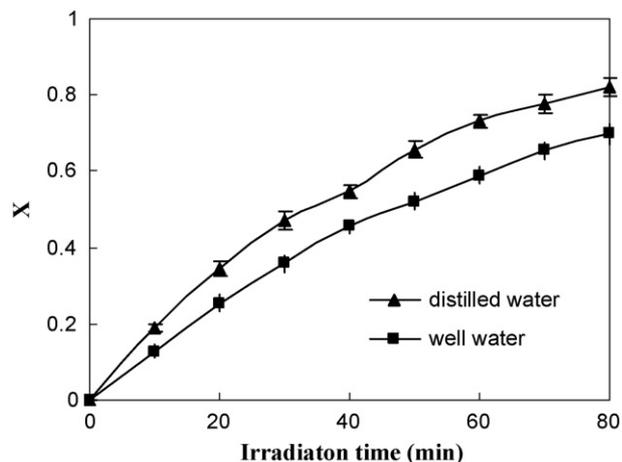| Characteristics	Value
pH	7.8
Specific conductivity (mS cm^{-1})	0.885
Total hardness (mg l^{-1} CaCO$_3$)	272.5
Calcium hardness (mg l^{-1} CaCO$_3$)	200
Carbonate hardness (mg l^{-1} CaCO$_3$)	88
Sulphate concentration (mg l^{-1} SO$_4{}^{2-}$)	172.8

Fig. 6. Investigation the efficiency of UV/ZnO process in removal of diazinon from real water. [diazinon]$_0$ = 20 mg l^{-1}; [ZnO]$_0$ = 150 mg l^{-1}.

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 decrease of degree photodegradation 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. pH real water containing diazinon decreases from 7.8 to 7.3 after photocatalytic oxidation of diazinon in the presence of ZnO, probably because of formation of CO$_2$. Specific conductivity of solution increased from 0.885 to 0.968 after performance UV/ZnO process. This increase can be attributed to formation of inorganic ions such as SO$_4{}^{2-}$, PO$_4{}^{3-}$ and NO$_3{}^-$ after photocatalytic degradation of diazinon. The concentration of sulphate reached 181.6 from 172.8 mg l^{-1} after operation.

3.6. Comparison of photocatalytic activity of prepared and commercial ZnO nanocrystals

Fig. 7 shows the photodegradation results in the presence of prepared and commercial ZnO. The results of Fig. 7 gave us the
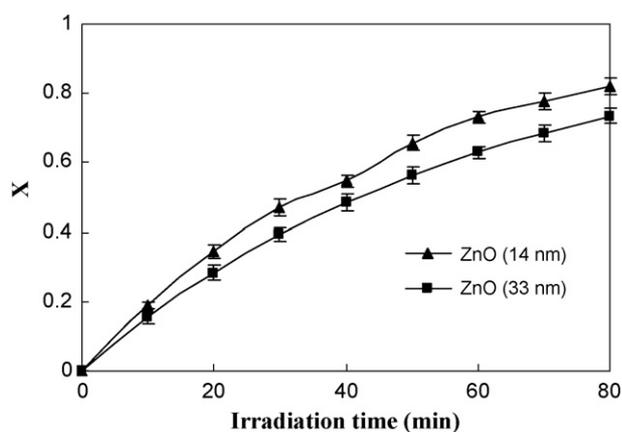

Fig. 7. Comparison of photodegradation efficiency of diazinon in the presence of prepared and commercial ZnO. [diazinon]$_0$ = 20 mg l^{-1}; [ZnO]$_0$ = 150 mg l^{-1}; pH neutral.
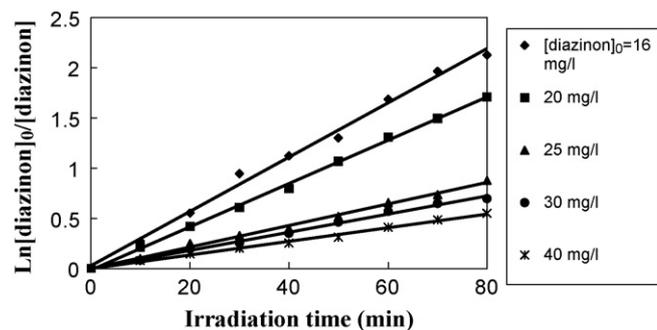
Fig. 8. Determination of the pseudo-first-order kinetic rate constant, k_{obs}.
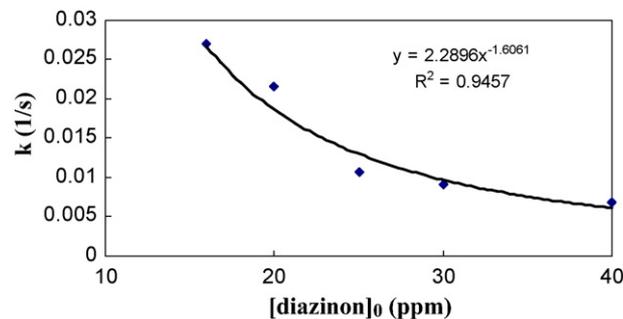

Fig. 9. Pseudo-first-order degradation rate constant of diazinon as a function of initial concentration of diazinon. $[ZnO]_0 = 150 \, mg \, l^{-1}$; pH neutral.

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 two reasons. (1) 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. (2) Comparing specific surface of two samples ZnO, it can be seen that BET is closely related to the mean size of sample particles. The surface area of ZnO photocatalyst will increase as the size of ZnO crystals decreases, which will promote the adsorption of more insecticide molecules on the surface [32]. Difference in photocatalytic degradation efficiency, two samples, may also arise from having difference in morphology.

3.7. Kinetics of photocatalytic degradation of diazinon

Photodegradation experiments of diazinon by UV/ZnO process exhibited pseudo-first-order kinetics with respect to the concentration of the organic compound:

$$-\frac{d[\text{diazinon}]}{dt} = k_{obs}[\text{diazinon}] \qquad (19)$$

Whose integration gives, for $[\text{diazinon}] = [\text{diazinon}]_0$ at $t = 0$:

$$\ln\left(\frac{[\text{diazinon}]_0}{[\text{diazinon}]}\right) = k_{obs}t \qquad (20)$$

In which k_{obs} is the pseudo-first-order rate constant.

Fig. 8 shows a plot of $\ln([\text{diazinon}]_0/[\text{diazinon}])$ versus time for all the experiments with different initial concentration of diazinon. By applying a least square regression analysis the values of k_{obs} have been obtained. Table 3 reports the values of k_{obs}, degree of photodegradation after 50 min and R (liner cor-

relation coefficient)-squared for all experiments carried out. The reaction rate proceeds according to pseudo-first-order kinetics with a kinetic constant, 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. The pseudo-first-order kinetic constant of reaction could be correlated to $[\text{diazinon}]_0$ by

$$k = 2.2896[\text{diazinon}]_0^{-1.6061} \qquad (21)$$

A good correlation was indicated in the plot of Fig. 9.

The photodegradation of diazinon in the presence of UV/ZnO could be predicated by

$$\frac{C}{C_0} = \exp(-2.2896[\text{diazinon}]_0^{-1.6061})t \qquad (22)$$

After incorporating the original data and modeled data into Fig. 10, the modeled curve fit quite well to the real data, indicating this approach provides an efficient method to have a quick prediction of insecticide decay in UV/ZnO process with various insecticide dosages.

3.8. Comparison of the quantum yield for both direct photolysis and photocatalysis

The quantum yield is a useful parameter in indicating the efficiency of a photodegradation reaction, and is defined as the
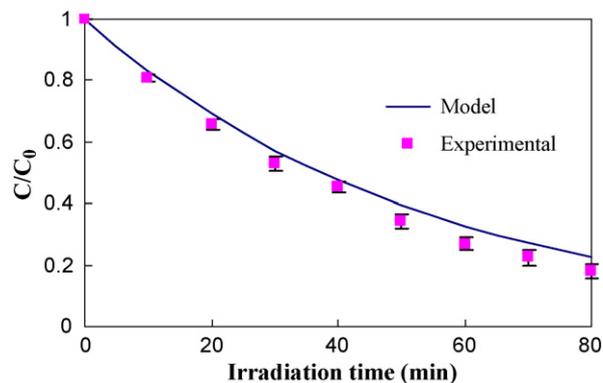
Table 3
Diazinon conversion (at 50 min) and pseudo-first-order kinetic rate constant in photocatalytic experiments with different initial concentration

Experiment number	$[ZnO]_0$ (mg l^{-1})	$[\text{diazinon}]_0$ (mg l^{-1})	X_5	k_{obs}	R^2
1	150	16	0.86	0.027	0.98
2	150	20	0.66	0.0215	0.99
3	150	25	0.41	0.0107	0.99
4	150	30	0.37	0.0091	0.99
5	150	40	0.27	0.0068	0.99

Fig. 10. Comparison of original data and modeled data. $[\text{diazinon}]_0 = 20 \, mg \, l^{-1}$; $[ZnO]_0 = 150 \, mg \, l^{-1}$; pH neutral.

Table 4
Photodecay quantum yield of diazinon at 253.7 nm (the molar absorptivity of diazinon at 253.7 nm is 3558 mol^{-1} l cm^{-1} and light intensity = 2.33 × 10^{-6} Einstein l^{-1} s^{-1} and l = 1.4 cm)

Process	Quantum yield
UV	0.0007
UV/ZnO (33 nm)	0.010
UV/ZnO (14 nm)	0.013

Table 5
The E_{EO} values for photodegradation of diazinon ([diazinon]$_0$ = 20 ppm, [ZnO] = 150 ppm, pH neutral)

Process	E_{EO} (kWh m^{-3})
UV	20,000
UV/ZnO (33 nm)	1388.8
UV/ZnO (14 nm)	1075.3

number of molecules being decomposed per photon absorbed [33]:

$$\varphi = \frac{\text{Number of molecules reacted (or produced)}}{\text{Number of photons of light absorbed}} \quad (23)$$

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. (24) [34]:

$$\varphi = \frac{k}{2.303 I_{0,\lambda} \varepsilon_\lambda l} \quad (24)$$

where k (s^{-1}) is the pseudo-first-order rate constant, φ the quantum yield, $I_{0,\lambda}$ (Einstein l^{-1} s^{-1}) the incident light intensity at wavelength λ, ε_λ (cm^{-1} mol^{-1} l) the molar absorptivity at wavelength λ, and l is the cell path length (cm). The molar absorptivity, ε_λ, was calculated by the Beer–Lambert law from the measurement of absorbance at different diazinon concentrations.

The results of diazinon decay quantum yield through either direct photolysis or photocatalysis under the illumination of UV at 253.7 nm are presented in Table 4. The results showed 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. It is also found that the photocatalysis process in the presence of ZnO with mean size 14 nm offered the highest quantum yield.

3.9. Electrical energy efficiency

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 guality 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. Therefore, Bolton et al. defined the figure-of-merit "electrical energy per mass" (E_{EM}) for use in the zero-order kinetic regime and "electrical energy per order" (E_{EO}) for use in the first-order kinetic regime of AOPs [35]. This concept was accepted by the IUPAC as a technical report. 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 equation for a batch type reactor [36,37]:

$$E_{EO} = \frac{P \times t \times 1000}{V \times 60 \times \log(C_0/C)} \quad (25)$$

where P is the input power (kW) to the AOP system, t the irradiation time (min), V the volume of water (l) in the reactor, and C_0 and C are the initial and final pollutant concentrations, respectively. The E_{EO} values were obtained from the inverse of the slope of a plot of $\log(C_0/C)$ versus energy dose (kWh m^{-3}). The E_{EO} values are presented in Table 5. 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.

4. Conclusion

Effective degradation of diazinon, an insecticide, is possible by photocatalysis in the presence of prepared ZnO nanocrystals and UV light. The results indicated that degree of degradation of diazinon was obviously affected by illumination time, pH, insecticide concentration and photocatalyst amount. We also learned that optimal amount of photocatalyst was 150 ppm, with insecticide concentration of 20 ppm. 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. The results indicaed that the photocatalysis process in the presence of ZnO with mean size 14 nm offered the highest quantum yield.

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