INFLUENCE OF INORGANIC OXIDANTS AND METAL IONS ON PHOTOCATALYTIC ACTIVITY OF PREPARED ZINC OXIDE NANOCRYSTALS

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ABSTRACT

Zinc oxide nanocrystals were prepared by precipitation method using $ZnSO_4.7H_2O$ and NaOH as raw materials. The prepared ZnO nanocrystals were characterized by powder X-ray diffraction (XRD). Primary objective was to focus on the influence of inorganic oxidants, metal ions and anions on photocatalytic activity of prepared ZnO nanocrystals. The study on the effects of oxidants such as IO_4^-, $S_2O_8^{2-}$, BrO_3^- and ClO_3^- reveal that periodate ion is more efficient than others in improving the photocatalytic properties of ZnO nanocrystals. An investigation on the influence of metal ions on photocatalytic activity reveals that the removal of pollutant increases in the presence of Fe^{3+} and Cu^{2+}. But negative effects are observed in the presence of anions. The possible roles of the additives on the reaction and the possible mechanisms of effect were discussed. The quantum yield (φ) and electrical energy per order (E_{EO}) were estimated and compared for UV/ZnO/Oxidant catalytic system.

KEYWORD: ZnO, Photocatalysis, electrical enrgy, quantum yield, metal ions, oxidants.

1. INTRODUCTION

The unique and fascinating properties of nanostructures materials have triggered tremendous motivation among the scientist to explore the possibilities of using them in a wide range of possible application such as photoelectronic energy conversion materials (Ishibashi and Fujishima 2000, Litter 1999) and water or air purification as friendly environmental photocatalysts (Evgenidou *et al.*, 2005; Behnajady *et al.*, 2006).

One material that has been in great interest from wide range of technological field associated with nanotechnology is zinc oxide (ZnO) (Guo *et al.,* 2002). ZnO has been used in various applications such as photo-electric devices (Purica *et al.,* 2001), electronic devices (Aoki *et al.,* 2000), surface acoustic wave devices (Gorla *et al.,* 1999), field emitters (Jo *et al.,* 2003), sensors (Baruwati *et al.,* 2006), ultraviolet lasers (Yan *et al.,* 2003) and solar cells (Senoussaoui *et al.,* 2004).

Also Zinc oxide, a II-VI semiconductor material with a large direct band gap (3.37 eV) and a relatively high exciton binding energy (60 meV) at room temperature, has attracted considerable attention with respect to the degradation of various pollutants such as acid red 18 (Sobana and Swaminathan 2007), 4-nitrophenol (Parida *et al.,* 2006), acridine orange (Pare *et al.,* 2008), azo dye (Zhang *et al.,* 2008) and so on, due to its being relatively cheap, chemical stability and high photocatalysis (Hong *et al.,* 2006). However, the high degree of recombination of photogenerated electrons and holes in semiconductors decreased greatly their photocatalytic efficiency and impeded the practical application of photocatalytic technique in the degradation of contaminants in water and air. Thus, a major challenge in heterogeneous photocatalysis is the need to increase the charge separation efficiency of the

photocatalyst and its photocatalytic efficiency. Therefore, the new developments of this technology have focused on searching for suitable compounds to enhance the photodegradation rates of organic substrates by quenching the conduction band electrons. The use of inorganic oxidants, for examples $S_2O_8^{2-}$, IO_4^-, BrO_3^- and ClO_3^- in UV/photocatalyst system could increase the quantum efficiencies either by inhibiting electron-hole pair recombination through scavengering conduction band electrons at the surface of photocatalyst or offering additional oxygen atom as an electron acceptors to form the superoxide radical ion ($O_2^{\bullet-}$). It has been observed that additional of some metal ions to aqueous photocatalyst dispersions improve UV/photocatalyst system's power in degradation of organic substrates.

In this research, we selected insecticide diazinon as the deputy of organic pollutants. Diazinon is an organophosphorous insecticide with wide spread agricultural and non-agricultural uses, acting by inhibition of acetylcholinesterase (Kouloumbos *et al.,* 2003).

For practical application of wastewater treatment by UV/ZnO process, there is a need to determine the optimal conditions of experimental parameters for economic removal of the pollutant. Earlier, we have reported the effects of various parameters on the photocatalytic degradation of diazinon by UV/ZnO process (Daneshvar *et al.,* 2007). From the previous studies, the optimum technological conditions for photocatalytic degradation of insecticide were obtained. Till now, many methods have been developed to synthesize zinc oxide nanocrystals including vapor phase growth (Sun *et al.,* 2004), vapor-liquid-solid process (Gao and Wang 2004), sol - gel process (Kamalasanan and Chandra 1996), hydrothermal synthesis (Baruwati *et al.,* 2006), flame spry pyrolysis (Mueller *et al.,* 2003), thermal decomposition method (Yang and Chen 2004) and electrochemical deposition technique (Zheng *et al.,* 2002). In the present work, we have successfully prepared the nanosized ZnO crystals by the precipitation method using sodium hydroxide as precipitating agent. Then, influences of inorganic oxidants, anions and metal ions on photocatalytic activity of prepared zinc oxide nanocrystals were investigated. The effectiveness of UV/ZnO/Oxidant systems in a laboratory-scale photoreactor will be compared by apparent quantum yield and electrical energy consumption. The possible roles of the additives on the reactions and the possible mechanisms of effect were discussed.

2. EXPERIMENTAL
2.1. Materials
Diazinon, an insecticide was purchased from Chem-service (USA) and used as received. The chemical structure of diazinon is given in Figure 1. The other chemicals used in this study such as $(NH_4)_2S_2O_8$, $KBrO_3$, $KClO_3$, KIO_4, Na_2CO_3, Na_2SO_4, $NaHCO_3$, $NaNO_3$, $NaCl$, $ZnSO_4.7H_2O$, $NaOH$, $FeCl_3.6H_2O$ and $CuCl_2$ were obtained from Merck Co. (Germany) and used as received. The distilled water used throughout the work.
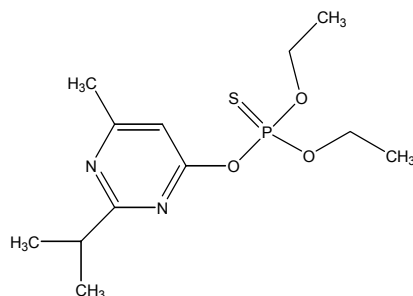

Figure 1. Chemical structure of insecticide diazinon (CAS number 333-41-5)

2.2. Preparation of zinc oxide nanocrystals
Nanometer oxide, ZnO, was synthesized using the precipitation method. $ZnSO_4.7H_2O$ 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 $100\,^\circ$ C in air to form the precursor of ZnO. Finally, the precursor was calcined in air at a certain temperature ($300\,^\circ$ C for 3 hours) to produce the nanosized ZnO photocatalyst.

Figure 2 illustrated the XRD pattern of ZnO nanocrystals prepared by precipitation method. The diffraction peaks of sample were quite similar to those of bulk ZnO, which can be indexed as the hexagonal wurtzite structure ZnO and diffraction data were in agreement with JCPDS card of ZnO (JCPDS card No. 36-1451). No peaks other than ZnO were detected. Thus, the results showed that single phase hexagonal ZnO can be obtained. The crystallite size measurement were also carried out using the Scherrer equation, $D = k\lambda / \beta \cos\theta$, where D is the crystallite size, k is a constant (= 0.89 assuming that the particles are spherical), λ is the wavelength of the X-ray radiation, β is the line width (obtained after correction for the instrumental broading), and θ is the angle of diffraction. The average particle size obtained from the XRD data is 14 nm.
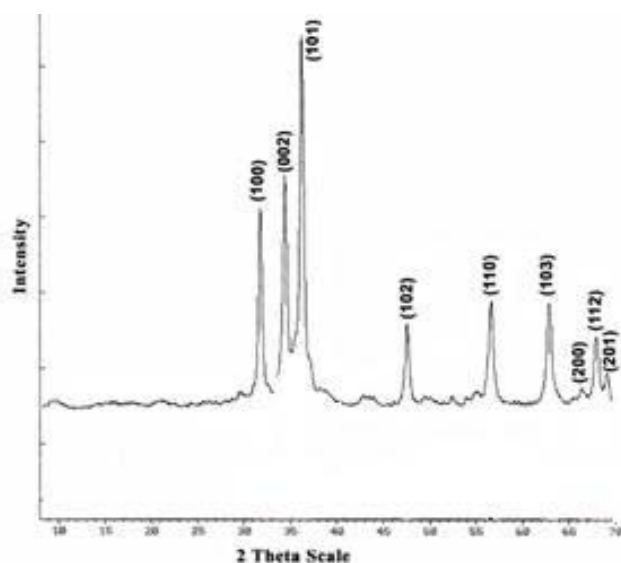

Figure 2. X-ray diffraction (XRD) pattern of synthesized ZnO nanocrystals

2.3. Procedure and analysis

At specific time intervals, suspension was sampled and samples were filtered through disks to remove ZnO nanoparticles. The concentration of insecticide in each sample was determined using a spectrophotometer (UV/Vis Spectrophotometer, Perkin-Elomer 550 SE) at λ_{max} =247 nm and a calibration curve. Pseudo-first-order reaction has been widely and successfully used for the description of photocatalytic degradation of organic pollutants (Wong and Chu, 2003). The removal rates of diazinon in UV/ZnO process is therefore expressed as:

$$-\frac{d[C]}{dt} = k[C] \quad \Leftrightarrow \quad -\ln(\frac{C}{C_\circ}) = kt \quad \Leftrightarrow \quad [C] = [C_\circ]\exp(-kt) \tag{1}$$

where ($C_\circ$) is the initial concentration of insecticide, (C) the concentration at timer t and k (min^{-1}) is the pseudo-first-order photocatalytic removal rate constant.

The half life time ($t_{1/2}$) of the first-order reaction is the time required for the reactants to be degraded to half of their initial concentrations. The relationship between $t_{1/2}$ and k is given by:

$$t_{\frac{1}{2}} = \frac{0.693}{k} \tag{2}$$

3. RESULTS AND DISCUSSION

3.1. Influence of inorganic oxidants

In the irradiated aqueous ZnO suspensions, oxygen on ZnO surface provides a natural sink for the photogenerated electrons. Hydroxyl radicals are then formed via the oxidation of ZnO

surface-sorbed H_2O or hydroxyl ions by the surviving holes. The introduction of a more effective electron acceptor than oxygen might be beneficial.

A group of oxidants utilized in this work is oxyhalogens, which have more than two oxygen atoms and one halogen atom (Cl, Br or I) at the center of the molecule. The high polarizability in these oxidants makes their central atom electropositive, so that they can capture the electrons ejected from ZnO.

3.1.1. Effect of addition of IO_4^- to ZnO

The effect of addition of periodate to ZnO for removal of the studied insecticide is shown in Figure 3. The enhancement of insecticide removal may be due to the scavenging of the photogenerated conduction band electrons of the excited ZnO which is more efficient than trapping with O_2 as follows (Irmak *et al.,* 2004):
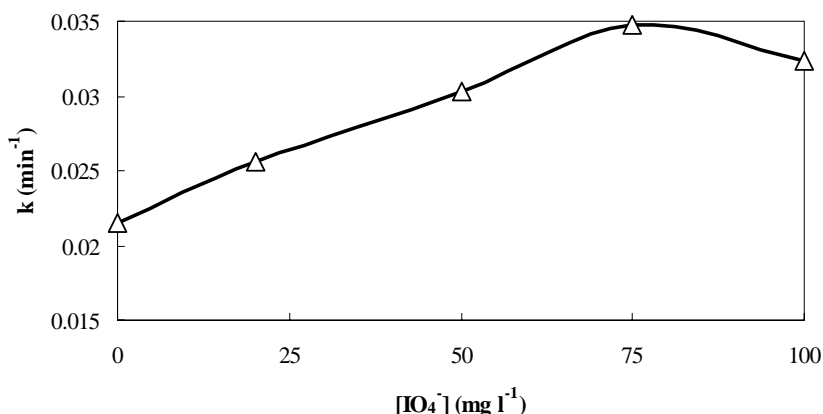
$$IO_4^- + 8\ e_{CB}^- + 8\ H^+ \rightarrow 4\ H_2O + I^- \tag{3}$$

Figure 3. Effect of IO_4^- addition on photocatalytic removal of insecticide
[ZnO]= 150 mg l^{-1}; [Diazinon]=20 mg l^{-1}; pH=neutral

Also the higher reactivity of UV/ZnO/IO_4^- is due to the production of high reactive intermediate radicals such as $IO_3^\bullet$, $OH^\bullet$ and $IO_4^\bullet$. These radicals also assisted the degradation by free radical pathways. The photolysis of periodate in aqueous solution have been extensively studied and the simple reaction scheme as shown in Table 1 has been suggested (Lee and Yoon 2004). On further increase of IO_4^- from 75 to 100 mg l^{-1} decreases the removal rate. This is due to adsorption effect of I^- ion on ZnO surface, which affects the catalytic activity of ZnO.

Table 1. Reaction mechanism for the periodate photolysis

Pathway I	Pathway II
$IO_4^-(I^{VII}) + h\nu \rightarrow IO_3^\bullet(I^{VI}) + O^{\bullet-}$	$IO_4^-(I^{VII}) + h\nu \rightarrow IO_3^-(I^{V}) + O(^3P)$
$O^{\bullet-} + H^+ \Leftrightarrow {}^\bullet OH$	$O_2 + O(^3P) \rightarrow O_3$
${}^\bullet OH + IO_4^- \Leftrightarrow OH^- + IO_4^\bullet$	
$O_3 + IO_3^\bullet \rightarrow IO_4^\bullet + O_2$	
$2IO_4^\bullet \Leftrightarrow I_2O_8$	
$I_2O_8 + H_2O \rightarrow IO_3^- + IO_4^- + 2H^+ + O_2$	
$2IO_3^\bullet \Leftrightarrow I_2O_6$	
$I_2O_6 + H_2O \rightarrow IO_4^- + IO_3^- + 2H^+$	

3.1.2. Influence of addition of BrO_3^- on ZnO

The enhancement of removal rate in the UV/ZnO/BrO_3^- system is due to the reaction between BrO_3^- and e_{CB}^-. The effect of addition of BrO_3^- on the photocatalytic removal of insecticide is shown in Figure 4. This reaction reduces the recombination of electron-hole pair (Poulios and Tsachpinis 1999).

$$BrO_3^- + 6e_{CB}^- + 6\ H^+ \rightarrow [BrO_2^-, HOBr] \rightarrow Br^- + 3H_2O \tag{4}$$
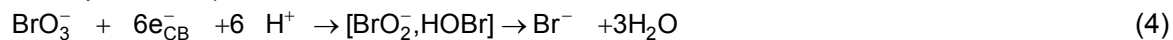
3.1.3. Effect of addition of ClO_3^- on ZnO

The effect of adding ClO_3^- on the photocatalytic removal of diazinon has been investigated by varying the amount of ClO_3^- from 0 to 100 mgl^{-1}. From Figure 5, it is clear that the addition of ClO_3^- increases the removal rate. The enhancement in UV/ZnO process by the addition of ClO_3^- is due to increased charge separation. This is done by accepting the conduction band electron (Choy and Chu, 2007).

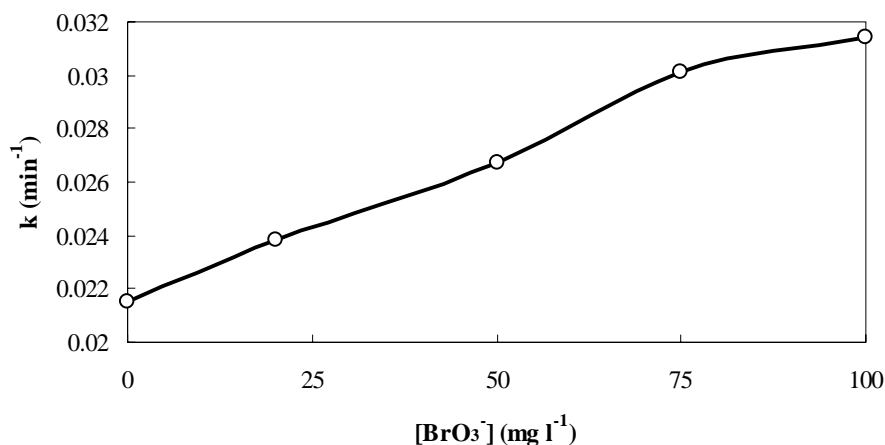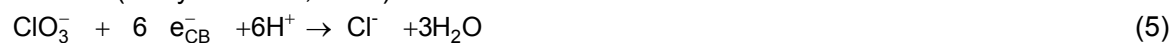$$ClO_3^- + 6\ e_{CB}^- + 6H^+ \rightarrow Cl^- + 3H_2O \tag{5}$$

Figure 4. Effect of BrO_3^- addition on photocatalytic removal of diazinon
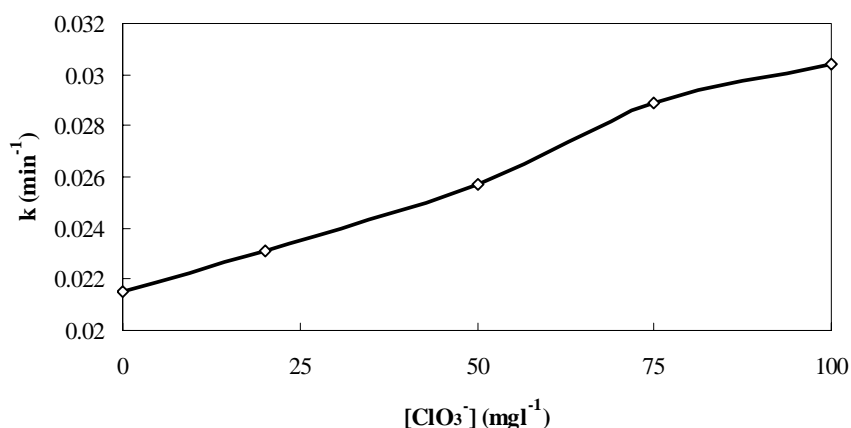[ZnO]= 150 mg l^{-1}; [Diazinon]=20 mg l^{-1}; pH=neutral

Figure 5. Effect of ClO_3^- addition on photocatalytic removal of diazinon
[ZnO]= 150 mg l^{-1}; [Diazinon]=20 mg l^{-1}; pH=neutral

3.1.4. Effect of addition of $S_2O_8^{2-}$ on ZnO

Figure 6 shows the effect of addition of peroxydisulfate to ZnO on removal of diazinon. The peroxydisulfate anions can trap the photogenerated conduction band electrons of ZnO more than O_2, and generate strong oxidizing $SO_4^{-\bullet}$ according to the following reaction (Sobana and Swaminathan 2007)

$$S_2O_8^{2-} + e_{CB}^- \rightarrow SO_4^{2-} + SO_4^{-\bullet} \tag{6}$$

Sulfate radicals anion is also generated at wavelength 254 nm and can participate in reactions with the solvent, according to the following reactions (Muruganandham and Swaminathan 2006)

$$S_2O_8^{2-} + hv \rightarrow 2\ SO_4^{-\bullet} \tag{7}$$

$$SO_4^{-\bullet} + H_2O \rightarrow {}^\bullet OH + SO_4^{2-} + H^+ \tag{8}$$

Sulfate radical does also react with H_2O_2 according to:

$$SO_4^{-\bullet} + H_2O_2 \rightarrow HSO_4^- + HO_2^{\bullet} \tag{9}$$
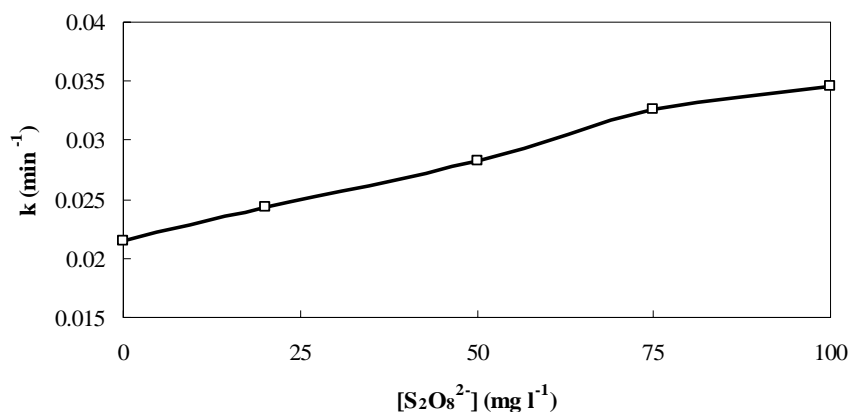
Figure 6. Effect of $S_2O_8^{2-}$ addition on photocatalytic removal of insecticide
[ZnO]= 150 mg l^{-1}; [Diazinon]=20 mg l^{-1}; pH=neutral

3.2 Effect of metal ions

The presence of dissolved metal ions is common in natural waters as well in industrial waters, and they can sensibly affect the rate and efficiency of photocatalytic reactions. The influence of added metal ions on photocatalytic removal is shown in Figure 7.
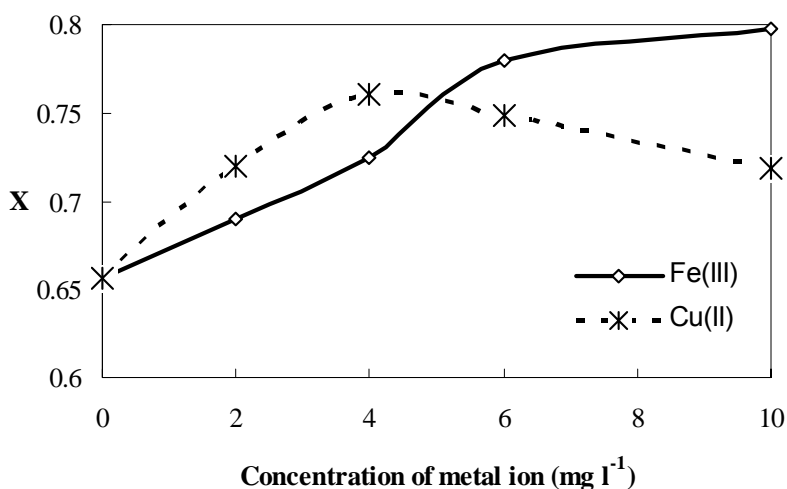
Figure 7. Effect of addition of metal ions on photocatalytic removal of diazinon
[ZnO]= 150 mg l^{-1}; [Diazinon]=20 mg l^{-1}; pH=neutral; Irradiation time=50 min

3.2.1 Effect of Cu^{2+}

The effect of adding Cu^{2+} on the photocatalytic removal efficiency of insecticide was investigated by varying the amount of Cu^{2+} from 0 to 10 mg l^{-1}. From Figure 7, it can be seen that adding a small amount of Cu^{2+} (up to 4 mg l^{-1}) the photocatalytic removal efficiency of diazinon increases from 0.65 to 0.76, but if the Cu^{2+} concentration is larger than 4 mg l^{-1}, the photocatalytic removal efficiency decreases. Cu^{2+} behaves as electron scavenger, preventing the recombination of electron-hole pairs, thus increasing the chances of the formation of $OH^{\bullet}$ on the ZnO surface (Ravichandran et al., 2007).

$$Cu^{2+} + e_{CB}^{-} \rightarrow Cu^{+} \tag{10}$$

This is favorable for the photocatalytic reactions. But when the Cu^{2+} concentration is higher, the photocatalytic removal efficiency decreases. It may be attributed to the low reduction potential for Cu^{2+}/Cu^{+} couple. As a result, Cu^{2+} ions are reduced to Cu^{+} by electrons. While Cu^{+} ions, thus formed are oxidized to Cu^{2+} by the photogenerated holes on the surface of ZnO nanoparticles or by $OH^{\bullet}$ through the following reactions (San et al., 2002).

$$Cu^{+} + h^{+} \rightarrow Cu^{2+} \tag{11}$$

$$Cu^{+} + OH^{\bullet} + H^{+} \rightarrow Cu^{+} + H_2O \tag{12}$$
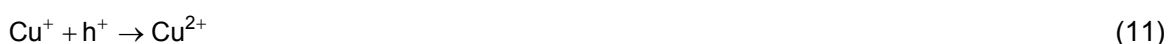
Therefore, above explanation Cu^{2+}-Cu^{+} cycle does not produce any $OH^{\bullet}$. Furthermore, it causes a decrease in the concentration of $OH^{\bullet}$ in the photocatalytic system.

3.2.2. Effect of Fe^{3+}

From Figure 7, it can be seen that adding a small amount of Fe^{3+} (0-10 mg l^{-1}) the removal efficiency of insecticide increases from 0.65 to 0.79. Positively charged Fe^{3+} adsorbed on the ZnO surface is easily reduced by trapping electrons and the amount of recombining electron-hole pairs thus decreases. It is favorable for the formation of $OH^{\bullet}$ on the surface of ZnO nanoparticles.

$$Fe^{3+} + e_{CB}^{-} \rightarrow Fe^{2+} \tag{13}$$
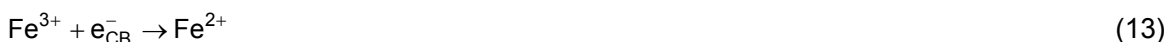
At the same time, there exist the following reactions:

$$Fe^{2+} + HO_2^{\bullet} + H^{+} \rightarrow Fe^{3+} + H_2O_2 \tag{14}$$

$$Fe^{2+} + H_2O_2 + H^{+} \rightarrow Fe^{3+} + OH^{\bullet} + H_2O \tag{15}$$

The above equations are favorable for the formation of $OH^{\bullet}$ (Chen and Liu, 2007). But when the Fe^{3+} concentration is higher, the Fe (OH)$^{2+}$ ion likely exists as the predominant monomeric iron (III)-hydroxy complex, which is also a major light absorbing species (Chen and Cheng 1999)

3.3 Influence of anions

Wastewater contains not only organic contaminants but also considerable amount of inorganic anions such as nitrate, sulfate, carbonate, etc. Hence it is useful to study the influence of these ions on this photocatalytic process. Two possible influences of inorganic ions on the photocatalytic reaction are: (1) changing the ionic strength of reaction medium and (2) inhibition of catalytic activity of the photocatalyst. The effects of added inorganic ions on the removal of diazinon are shown in Figure 8. The results clearly show that the addition of inorganic anions on the photocatalytic process decreases the removal rate. The inhibition effect of these ions is due to the reaction of these ions with holes and $^{\bullet}OH$ (Eqs. (16)-(23)) (Ravichandran et al., 2007 ; Daneshvar et al., 2007 ; Wenhua et al., 2000).
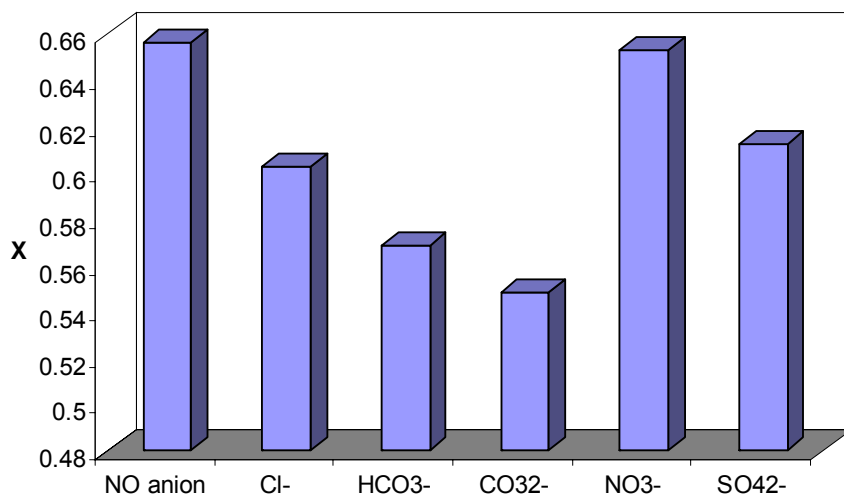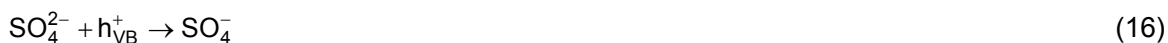
Figure 8. Effect of inorganic anions additions on the photocatakytic removal of insecticide.
[ZnO]= 150 mg l^{-1}; [Diazinon]=20 mg l^{-1}; pH=neutral; Irradiation time=50 min

$$SO_4^{2-} + h_{VB}^+ \rightarrow SO_4^- \tag{16}$$

$$SO_4^{2-} + {}^\bullet OH \rightarrow SO_4^{\bullet-} + OH^- \tag{17}$$

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

$$CO_3^{2-} + {}^\bullet OH \rightarrow OH^- + CO_3^{\bullet-} \tag{19}$$

$$Cl^- + h_{VB}^+ \rightarrow Cl^\bullet \tag{20}$$

$$Cl^\bullet + Cl^- \rightarrow Cl_2^{\bullet-} \tag{21}$$

$${}^\bullet OH + Cl^- \Leftrightarrow HOCl^{\bullet-} \tag{22}$$

$$HOCl^{\bullet-} + H^+ \rightarrow Cl^\bullet + H_2O \tag{23}$$

Addition of NO_3^- did not affect of the removal rate appreciably.

3.4 Quantum yield

The quantum yield of a reaction is defined as the number of diazinon molecules being decomposed per photon absorbed (Tsui and Chu 2001)**.**

$$\varphi = \frac{\text{Number of molecules decomposed}}{\text{Number of photons of light absorbed}} \tag{24}$$

The photo decomposed rate constants (k) of diazinon under the monochromatic light source can also be used for the calculation of its reaction quantum yield using Eq. (25))Choy and Chu 2007, Wong and Chu 2003).

$$\varphi = \frac{k}{2.303 I_\circ \varepsilon_\lambda l} \tag{25}$$

where φ is the reaction of quantum yield (dimensionless), I_o is the intensity of the incident light at 254 nm (2.33×10^{-6} Einstein l^{-1} s^{-1}), ε_λ is the molar absorptivity of diazinon at 254 nm (3558 mol^{-1} l cm^{-1}), l is the cell length (cm). The results of removal quantum yields by UV/ZnO/Oxidant are shown in Table 2.

3.5. Electrical energy per order

Although several reports are available in the literature on electrical energy determination of various AOPs, it is necessary to study the electrical energy consumption of the AOPs, under experimental conditions. Generally, the electrical energy consumption of AOPs, depends on number of experimental factors (type of pollutant being treated, configuration of the reactor, and type of light source used, etc.) and hence, electrical energy determination becomes important for the processes studied. A number of important factors such as economic, effluent quality, cost, etc., also play a vital role in selecting a waste treatment technology. Since

photodegradation of aqueous organic pollutant is an electrical energy- related process, the electrical energy represents a major fraction of the operating costs. The figures of merit E_{EO} allows for a rapid determination of the electrical energy cost and they indicate the total power required. For comparative purpose, the treatment efficiencies for UV/ZnO/Oxidant processes are evaluated through the E_{EO} values. The E_{EO} is defined as the number of kWh of electrical energy required to reduce the concentration of pollutant by one order of magnitude (90%) in 1 m^3 of contaminated water. The E_{EO} values were obtained from the inverse of the slope of a plot of log C/C_o versus UV dose. Considering first-order degradation kinetics, the UV doses were calculated for all processes using Eq. (26). From the UV doses, E_{EO} can also be calculated using Eq. (27) (Bolton *et al.,* 2001, Stephen *et al.,* 2000)

Table 2. Electrical energy per order and quantum yield for photocatalytic removal of insecticide by different systems

System	Concentration	$t_{1/2}$ (min)	E_{EO} (kWhm^{-3})	φ
UV	---	630	20000	0.0007
UV/ZnO	150 mg l^{-1}	32.23	1075.3	0.013
UV/ZnO (150 mg l^{-1})/ $S_2O_8^{2-}$	20 mg l^{-1}	28.4	944.26	0.015
	50 mg l^{-1}	24.48	814.13	0.0176
	75 mg l^{-1}	21.25	706.74	0.0203
	100 mg l^{-1}	20.03	665.89	0.0216
UV/ZnO (150 mg l^{-1})/ IO_4^-	20 mg l^{-1}	27.07	900	0.0159
	50 mg l^{-1}	22.87	760.39	0.0189
	75 mg l^{-1}	19.97	663.97	0.0216
	100 mg l^{-1}	21.39	711.1	0.0202
UV/ZnO (150 mg l^{-1})/ BrO_3^-	20 mg l^{-1}	29.11	968.06	0.0148
	50 mg l^{-1}	25.95	862.92	0.0166
	75 mg l^{-1}	22.94	762.91	0.0188
	100 mg l^{-1}	22.07	733.75	0.0195
UV/ZnO (150 mg l^{-1})/ ClO_3^-	20 mg l^{-1}	30.13	1001.74	0.0143
	50 mg l^{-1}	26.96	896.49	0.0160
	75 mg l^{-1}	24.06	800	0.0179
	100 mg l^{-1}	22.71	755.16	0.0190

$$UV\ dose = \frac{Lamp\ power(kW)\ \times\ Time\ (min) \times 1000}{Treated\ volume(l) \times 60} \tag{26}$$

$$E_{EO} = \frac{UV\ dose}{log\ (C_o/C)} \tag{27}$$

The results are presented in Table 2. The electrical energy consumption for insecticide diazinon is in the following order UV>UV/ZnO>UV/ZnO/ClO_3^-> UV/ZnO /BrO_3^-> UV/ZnO /$S_2O_8^{2-}$> UV/ZnO /IO_4^-. The higher electrical energy consumption means lower process efficiency. The E_{EO} values revealed that increase of rate constant lowers the consumption of electrical energy.

4. CONCLUSION
From this experimental study, several conclusions can be made:
1) Addition of oxidants such as $S_2O_8^{2-}$, IO_4^-, BrO_3^- and ClO_3^- increase the photocatalytic activity significantly.
2) Among the oxidants periodate ion is found to be more efficient than others.
3) Addition of Cu^{2+} and Fe^{3+} increased the photocatalytic removal of insecticide
4) The apparent quantum yield (φ) was calculated for UV/ZnO/Oxidant catalytic systems and was highest for periodate.

5) The EE/O values of UV/ZnO/Oxidant systems could be arranged as follow:

UV/ZnO/ ClO_3^- > UV/ZnO /BrO_3^- > UV/ZnO / $S_2O_8^{2-}$ > UV/ZnO /IO_4^- .

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