# Journal Pre-proof

The photocatalytic removal of diazinon from aqueous solutions using tungsten oxide doped zinc oxide nanoparticles immobilized on glass substrate

Afshin Maleki, Farzaneh Moradi, Behzad Shahmoradi, Reza Rezaee, Seung-Mok Lee

PII: S0167-7322(19)33991-1

DOI: https://doi.org/10.1016/j.molliq.2019.111918

Reference: MOLLIQ 111918

To appear in: Journal of Molecular Liquids

Received Date: 17 July 2019

Revised Date: 9 October 2019

Accepted Date: 11 October 2019

Please cite this article as: A. Maleki, F. Moradi, B. Shahmoradi, R. Rezaee, S.-M. Lee, The photocatalytic removal of diazinon from aqueous solutions using tungsten oxide doped zinc oxide nanoparticles immobilized on glass substrate, *Journal of Molecular Liquids* (2019), doi: https://doi.org/10.1016/j.mollig.2019.111918.

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2019 Published by Elsevier B.V.



1	The photocatalytic removal of diazinon from aqueous solutions using tungsten
2	oxide doped zinc oxide nanoparticles immobilized on glass substrate
3	Afshin Maleki <sup>1,*</sup> , Farzaneh Moradi <sup>1</sup> , Behzad Shahmoradi <sup>1</sup> , Reza Rezaee <sup>1</sup> , Seung-Mok Lee <sup>2,*</sup>
4	
5	<sup>1</sup> Environmental Health Research Center, Research Institute for Health Development, Kurdistan
6	University of Medical Sciences, Sanandaj, Iran.
7	<sup>2</sup> Department of Environmental Engineering, Catholic Kwandong University, Ganeung,
8	25601, Korea
9	*Corresponding authors: maleki43@yahoo.com, leesm@cku.ac.kr
10	

#### 11 Abstract

Diazinon is an important organophosphorus pesticide with extensive use, which is considered to 12 be a major health hazard for humans due to its adverse effects on cholinesterase activity and 13 central nervous system. The entry of diazinon into water resources affects a wide range of non-14 target organisms, which highlights the importance of its removal from water resources. The 15 present study aimed to synthesize and use WO<sub>3</sub> doped ZnO nanocatalyst to degrade diazinon. 16 17 Zinc oxide nanoparticles were synthesized using the hydrothermal method and doped with 0.5%, 1%, and 2% M tungsten oxide. Moreover, the effects of dopant percentage, pH, the initial 18 concentration of diazinon, nanoparticle dosage, and contact time were investigated. The results 19 of EDS revealed that W was doped into ZnO structure. The maximum diazinon degradation 20 (99%) was obtained using 10 mg/cm<sup>-2</sup> 2% WO<sub>3</sub> doped ZnO, 10 mg/l diazinon, neutral pH value 21 and contact time of 180 min. Removal efficiency was decreased by increasing pH and initial 22 diazinon concentration. The experimental kinetic data followed the pseudo-first order model. 23 The reaction rate constant (kobs) was decreased from 0.0205 to 0.0034 1/min with increasing 24 25 initial diazinon concentration from 10 to 200 mg/L, respectively. The figures of merit based on electric energy consumption (EEO) indicate that less energy is consumed during the degradation 26 of diazinon in the presence of 2% WO<sub>3</sub> doped ZnO compared with other photocatalysts. 27 Therefore, it could be concluded that 2%WO3 doped ZnO is a promising material for 28 photocatalytic degradation of diazinon with high efficiency under optimal condition. 29

30 Keywords: Pesticides, Zinc Oxide, Photocatalyst, Doping, Tungsten

#### 32 **1. Introduction**

Although two-thirds of the Earth is covered with water, water crisis remains a major concern in 33 human communities. As predicted by the United Nations, about 48 countries (approximately 34 32% of the world's population) will be faced with water scarcity by 2025 [1, 2]. Agricultural 35 wastewater is considered to be a major source of water pollution. According to the national 36 standards for water in Iran, approximately 30-35 billion cubic meters of agricultural wastewater 37 is generated annually, which contains various fertilizers, pesticides, and herbicides, and its 38 release into the environment leads to the contamination of surface water and groundwater [2, 3]. 39 Organophosphate pesticides are frequently used in various regions across the world. Many 40 pesticides are typically found in aquatic systems as a result of activities such as chemical 41 deposition, industrial wastewater, and agricultural runoff [4, 5]. Organophosphate pesticides are 42 43 hazardous to human health due to their high shelf life, stability, and toxicity [6, 7].

Diazinon<sup>1</sup> is an organophosphorus pesticide, which has long been utilized used as a miticide, 44 insecticide, and nematicide and is classified as a relatively hazardous toxin (class II) by the 45 World Health Organization (WHO) [4, 7, 8]. Low concentrations of diazinon (even 350 ng/l) 46 could be highly toxic to aquatic organisms [9, 10]. According to the literature, lethal doses of 47 48 diazinon for humans are within the range of 90-444 mg/kg [10]. The United States Environmental Protection Agency (USEPA) has determined the level of diazinon in drinking 49 50 water to be 0.6 µg/l so as to prevent the adverse effects of this compound on human health, especially in elderly adults (aged 70 years) [3]. Diazinon and its metabolites with widespread 51 agricultural and non-agricultural uses, have been identified in the environment worldwide [11]. It 52 53 enters the environment through human activity and, thus, is most frequently detected in water as a main synthetic emerging water contaminant [12]. More than 13 million pounds of diazinon is 54 used in the United States annually [13]. Therefore, the release of this compound into 55 groundwater is a major concern [13]. Important environmental concerns associated with its use 56 include bird killing, surface water pollution and impacts on aquatic species [14]. Since diazinon 57 is the most widely used and most dangerous pesticide for the environment, thus, in order to 58 protect human health, diazinon should be removed from contaminated water before consumption 59 [12, 13]. Therefore, using effective chemical and biological methods to eliminate these pesticides 60 from water and wastewater is very important [10]. 61

<sup>&</sup>lt;sup>1</sup> (O,O-diethyl-O-[6-methyl-2-(1-methylethyl)- 4-pyrimidinyl] phosphorothioate)

#### Journal Pre-proof

Several methods have been proposed for the removal of diazinon, including ultrafiltration, 62 reverse osmosis, photocatalytic processes and adsorption by magnetic nanoparticles, chemical 63 coagulation, membrane processes, and biological methods [2, 4, 10]. Among the available 64 methods for the removal of toxic compounds, advanced oxidation processes are considered 65 superior; such examples are ultraviolet radiation, ozone application, Fenton reaction, and use of 66 nanocatalysts [4, 15-18]. Photocatalytic degradation has attracted the attention of researchers 67 within the past two decades, which involves the use of semiconductor metal oxides for 68 environmental protection [19]. 69

70 Various metal oxides have been used as active photocatalysts for the photocatalytic degradation of organic and inorganic pollutants, such as titanium, tungsten oxide, zinc oxide, iron oxide, 71 72 cadmium sulfide, and zinc sulfide [19, 20]. Among these metal oxides, zinc oxide and titanium 73 dioxide have been extensively utilized as photocatalysts for the removal of various contaminants 74 owing to their high light sensitivity and wide-bandgap energy [21]. These remarkable properties 75 allow the enhancement of oxidation and reduction processes more rapidly compared to other metal oxide semiconductors. Zinc oxide is reported to be an efficient photocatalyst for the 76 destruction of various contaminants with its special properties, such as chemical stability, 77 78 nontoxicity, significant optical and electrical properties, and remarkable oxidizing properties. However, the photocatalytic activity of zinc oxide is limited to the ultraviolet light range of the 79 80 solar energy spectrum due to its high bandgap energy (3.37 eV) [22]. Considering that only 5-7% of the sunlight's energy is in the form of ultraviolet light, this small amount limits the use of 81 sunlight as a natural source of light. Another limitation in this regard is the rapid recombination 82 83 of the electron/hole cavity generation, agglomeration, and poor dispersion [19, 23-25]. Therefore, these limitations should be overcome in order to improve the activity and efficiency 84 of zinc oxide by changing its structure using dopants and surface modifiers. Use of surface 85 modifiers, surfactants or organic ligands has proven effective in overcoming the mentioned 86 limitations. It is also notable that the doping of nanoparticles causes changes in the bandgap 87 energy, and thus shifting the absorption band to the visible region in semiconductor systems [26, 88 27]. Metal ions act as traps for the produced electrons through replacement in the structure of 89 zinc oxide and preventing the rapid recombination of electrons/hole cavities, thereby increasing 90 photocatalytic activity compared to pure zinc oxide [28]. Therefore, the doping of zinc oxide 91 nanoparticles using proper dopants with narrow bandgap energy could decrease the bandgap 92

#### Journal Pre-proo

energy, making it suitable for the optical analysis of organic and toxic pollutants [19, 29]. 93 Tungsten oxide is considered to be a viable option for doping. The bandgap energy of tungsten 94 oxide is 2.8 eV, which could activate the zinc oxide bed. Tungsten oxide is a new semiconductor 95 with narrow bandgap energy, which is effectively activated with sunlight illumination and acts as 96 a photocatalyst for active light [30]. In addition, it has high stability and efficacy in the 97 destruction of natural and artificial contaminants. On the other hand, when tungsten oxide is used 98 separately, its photocatalytic activity is weak compared to other metal oxides due of its relatively 99 low conduction band level [31]. Therefore, if it is to be used as a photocatalyst, its activity 100 101 should be enhanced. For instance, studies have indicated that tungsten oxide powder could be utilized as a photocatalyst with trivalent iron or silver in the presence of visible light in the 102 oxidation process of pollutants [19, 32]. As a general conclusion and milestone of this study, it 103 104 can be stated that although zinc oxide is a common photocatalyst with excellent photocatalytic 105 activity and also high physical and chemical stability but it also has some drawbacks such as being activated by ultraviolet light due to its wide band gap [26]. Therefore, appropriate 106 modifications to the structure of zinc oxide are necessary in order to be activated by visible light 107 or a low-intensity source of UV light. In fact, ongoing research on photocatalysts are directed 108 109 toward modifying the characteristics of ZnO to extend its light absorption edge to a higher wavelength and lower intensity and also in terms of lower energy consumption, easy production 110 and high usage of light source [33]. Numerous methods and strategies have been employed to 111 achieve this goal until now. However, the most effective and direct routes for improving the light 112 absorption edge of ZnO is structure control especially band gap regulation through elemental 113 doping [33]. There are various methods for ZnO doping, among them the hydrothermal method 114 is noticeable due to its simple process, environmental compatibility and mild preparation 115 conditions [34]. In addition, more attention has been paid recently to mixed oxide 116 semiconductors because it has been found that an efficient charge separation will be achieved by 117 coupling two semiconductor particles with different energy levels [35]. For this reason, WO<sub>3</sub> 118 coupling is considered to improve the photocatalytic activity of ZnO in this study because  $WO_3$ 119 with an energy gap of 2.8 eV can function as an electron accepting species through a type II 120 heterojunction [35]. Despite numerous studies about doped ZnO photocatalysts and also partly 121 about W-doped ZnO, there has been little research exploring WO<sub>3</sub>-doped ZnO. Ramos-Delgado 122 et al. [36] reported solar photocatalytic degradation of malathion pesticide with illuminated 123

WO3/TiO2 prepared by sol-gel method. To the best of our knowledge, there is no research study 124 on the removal efficiency of diazinon with WO<sub>3</sub> doped ZnO nanocatalysts synthesized by 125 hydrothermal method. Moreover, optimal values of affecting parameters in this process have 126 been paid less. Considering that photocatalysts are often used in the form of suspensions, their 127 separation from aqueous suspensions is considered to be a hazardous operation in terms of 128 health. On the other hand, the separation of nanocatalysts particles from the effluent is difficult 129 and considered as a drawback especially in the practical photocatalytic process [37]. Therefore, 130 there are ongoing efforts to find cost-effective ways to address this problem. So immobilization 131 of the catalyst in the solid support (without the loss of their photocatalytic properties) to reduce 132 the release of nanoparticles is another highlight of this study. Therefore, the WO<sub>3</sub> doped ZnO 133 nanoparticles were first synthesized via mild hydrothermal conditions method; then, in order to 134 prevent the release of the nanoparticles in the effluent, immobilization of the nanoparticles on the 135 136 glass was done. Effect of solution pH, catalyst dosage, initial diazinon concentration, Light Intensity, Dopant Percentage, and Contact Time on the photocatalytic degradation of diazinon 137 was investigated. Finally, kinetic parameters for the photocatalytic degradation were obtained by 138 application of the Langmuir–Hinshelwood (L–H) model. The electrical energy per order (EEo) 139 140 was calculated to evaluate cost efficiency of the processes.

- 141
- 142 **2.** Materials and Methods

#### 143 **2.1.** Chemicals

This quasi-experimental study was conducted on a laboratory scale. All the chemicals were obtained from Merck Company (Germany), and tungsten oxide and standard diazinon were purchased from Sigma-Aldrich (USA). Table 1s (supplementary) shows the chemical and structural properties of diazinon. It is notable that all the utilized materials were of the laboratory grade.

149

#### 150 2.2. Applied Reactor

In this study, a Plexiglas reactor (500 mL) was used as the batch system (Figure 1). In order to provide the required energy, five six-Watt ultraviolet lamps (Phlips Co., the Netherlands) with the length of 21 centimeters were used. The lamps were installed on the upper segment of the reactor, and the glass plate containing the nanoparticles (surface area: 200 cm<sup>2</sup>) was placed horizontally inside the reactor in direct contact with the contaminant. The intensity of theultraviolet lamps was measured using a UV meter.



Fig. 1. Schematic representation of the reactor used in the photocatalytic degradation of diazinon

160

#### 161 2.3.Synthesis of Zinc Oxide and its Doping with WO<sub>3</sub>

162 ZnO nanoparticles were synthesized using a very simple hydrothermal method. This method has no complexity and this simplicity is its major advantage. To this end, the initial zinc oxide was 2 163 N ZnO, and the concentrations of 0.5%, 1%, and 2% of tungsten oxide (as a dopant) were poured 164 into a Teflon liner ( $V_{fill} = 10$ -mL). Following that, 10 milliliters of 1 N sodium hydroxide and 0.5 165 milliliter of surfactant were added to the mixture, and the Teflon liner was placed in an autoclave 166 at the temperature of 120°C for 12 hours. Because one of the drawbacks of nanoparticles is their 167 agglomeration and low dispersion in the medium used. So to overcome these issues, surface 168 modification has been introduced and applied as a novel approach in this case. Therefore, 169 170 applying appropriate surface modifiers (such as surfactants) with the desired volume can alleviate such problems [38]. After the synthesis, the nanoparticles were washed several times 171 with double distilled water and stored at the desiccator after drying at laboratory temperature 172 [39]. In order to confirm the synthesis of the nanoparticles, the other properties of the 173 nanoparticles were examined as well. 174

175

## 176 2.4.Immobilization of the Nanoparticles on Sandblasted Glass

The immobilization of the nanoparticle was carried out on sandblasted glass (thickness: 4 mm).
To do so, the sandblasted glass was placed in 50% sodium hydroxide for 24 hours and washed

and dried afterwards. At the next stage, the zinc oxide nanoparticles that were doped with 179 various concentrations of tungsten oxide were expanded on the glass. Afterwards, the glass was 180 dried in an oven at the temperature of 100°C. It was then placed in the furnace at 500 °C for 2 h 181 to stabilize the nanoparticles. [40, 41]. 182

183

#### 184

#### 2.5. Characterization of the Synthesized Nanoparticles

Fourier transform- infrared (FTIR), Powdered X-ray diffraction (PXRD), scanning electron 185 microscopy (SEM), atomic force microscopy (AFM), **Energy-dispersive** X-ray 186 spectroscopy (EDS) and Zeta potential studies were used to determine the properties of tungsten 187 oxide-doped zinc oxide nanoparticles. Accordingly, the Tsarn SEM (MIRA3, the Czech 188 Republic) was applied to describe the morphology and size of the WO<sub>3</sub>-doped zinc oxide 189 190 nanoparticles, and an Inel XRD (EQUINOX 3000, France) was used to assess the crystalline structure and crystalline nanoparticle lattice. In addition, the Bruker FTIR (Tensor 27, Germany) 191 was employed to determine the functional groups that were generated at the nanoparticle level, 192 and AFM (Advance, Iran) was used to determine the specifications of the nanoparticle surface. 193 Finally, the particle size and distribution, as well as the electrical potential of the nanoparticle 194 195 surface, were evaluated using dynamic light scattering (DLS) and a zeta potential analyzer (Nanobrook Omni, USA). 196

197

#### 2.6. Experiments 198

To evaluate the operational parameters affecting the photocatalytic process of diazinon removal, 199 200 the influential factors in the process were investigated, including the pH (3, 5, 7, 9, and 11), initial light intensity (6, 18, and 30 Watts), amount of nanoparticles per unit area of the glass (2, 201 6, and 10 mg/cm<sup>2</sup>), diazinon concentration (10, 20, 50, 100, and 200 mg/l), and contact time (20, 202 10, 30, 45, 60, 90, 120, and 180 minutes). Diazinon concentrations were also assessed using 203 standard methods. To this end, gas chromatography (CP-3800 VARIAN) was used with an FID 204 detector and CP-Sil8-CB column. Finally, the removal rate of diazinon was determined using 205 Equation 1 [16], which was developed based on the samples before and after the removal 206 207 efficiency [37], as follows:

$$R = \left[1 - \frac{C_{out}}{C_{in}}\right] \times 100 \tag{1}$$

where R% is the removal rate of diazinon (%),  $C_{in}$  represents the initial concentration of diazinon (mg/l), and  $C_{out}$  shows the final concentration of diazinon (mg/l). The kinetics of the photocatalytic degradation of diazinon has been modeled using the equation of Langmuir-Hinshelwood (L-H) and figure-of-merit (FOM) of the process was determined based on electric energy consumption according to the method introduced by the Photochemistry Commission of the International Union of Pure and Applied Chemistry (IUPAC) [42].

214 215

216

## 3. Results and Discussion

## 3.1. Characterization of the Undoped Zinc Oxide and WO<sub>3</sub>-doped Zinc Oxide

Figure 2 shows the SEM images of the pure zinc oxide nanoparticles and those that were doped 217 with various molar percentages of tungsten oxide. Evidently, the nanosized form was hexagonal, 218 confirming the proper synthesis of zinc oxide. In terms of the morphology, the particles were 219 almost separate with slight agglomeration. Figure 2e and f depict the mean particle size, which 220 evidently reduced. Therefore, the mean particle size of the zinc oxide doped with 2% tungsten 221 222 oxide was estimated at 48.49 and 27.911 nanometers, respectively, while the mean particle size of the pure zinc oxide was calculated to be 156.68 and 68.63 nanometers, respectively. The 223 synthesis of WO<sub>3</sub> doped ZnO nanocatalysts is confirmed by the EDS analysis. Figure 3a and 3b 224 show the EDS spectra of pure ZnO and WO<sub>3</sub> doped ZnO. According to Figure 3a, there are two 225 elements, including Zn and O, in pure ZnO. But in the structure of zinc oxide there are three 226 227 compounds, including oxygen, tungsten and zinc (Figure 3b).

Journal Pre-proof



229

Fig.2. SEM images and size distribution of the synthesized nanoparticles (a. 0.5 % WO<sub>3</sub> doped
ZnO; b. 1 % WO<sub>3</sub> doped ZnO; c & f 2 % WO<sub>3</sub> doped ZnO; d & e pure ZnO)
232
233



Fig. 3. EDSspectra of (a) pureZnO and (b) %WO3 doped ZnO.

Figure 4 shows the FTIR spectra of zinc oxide and WO<sub>3</sub> doped ZnO nanoparticles. As can be 237 seen, a strong bond was observed in the area of 469 cm<sup>-1</sup>, which was related to the Zn-O 238 stretching frequency [43]. Moreover, the stretching bond of the C=O of the organic matter was 239 observed at the wavelength of 1,730 cm<sup>-1</sup>. The stretching vibrations of the N-H observed at 3,448 240 cm<sup>-1</sup> were related to the N-H bond of the amine groups, which was obtained with the addition of 241 the *n*-butyl amine surfactant. Overall, the wavelength range of 1600-400  $\text{cm}^{-1}$  confirmed the Zn-242 O stretching bond, while the range of 3600-3400 cm<sup>-1</sup> was attributed to the presence of the N-H 243 bond [44]. The absorption band observed at 870 cm<sup>-1</sup> attributed to the W-O-W to the n(O–O) and 244 n(W-O-W) stretching of the bridging oxygen in WO<sub>3</sub>. The band seen at ~965 cm<sup>-1</sup> related to the 245 W=O and W–O in WO<sub>3</sub> [45, 46]. 246



250 The XRD pattern was used in order to assess the crystalline structure and purity of the 251 nanoparticles (Figure 5). The investigation of the XRD patterns of the pure zinc oxide and zinc 252 oxide nanoparticles doped with 0.5%, 1%, and 2% M of tungsten oxide indicated that the three 253 peaks of the patterns were (100), (002), and (101), which corresponded to the zinc oxide 254 crystalline structure on the Miller index. Based on this index and similar to the SEM images, the 255 256 hexagonal nanoparticles were confirmed in the XRD analysis. The sharp edges represented the crystallization of fine zinc oxide nanoparticles. The maximum intensity of the pattern in the 257 lattice (101) appeared at the angle of  $2\theta=36.045$  [47]. In the XRD pattern of the doped 258 specimens, no peak was added to the undoped samples, while the peak of the patterns had a 259 slight displacement, indicating the presence of tungsten. 260



Nanoparticles	a(A <sup>0</sup> )	c(A <sup>0</sup> )	Density g/cm³
Pure ZnO	3.2491	5.2071	5.6470
0.5 % WO₃ doped ZnO	3.2049	5.1216	5.9320
1% WO₃ doped ZnO	3.2190	5.1489	5.8490
2% WO₃ doped ZnO	3.1950	5.1027	5.9900

Table 1 shows the cell parameters and density of the nanoparticles. According to the information 268 in Table 1, the cell parameters of the zinc oxide nanoparticles doped with 2% tungsten oxide 269 reduced compared to the molar percentages of 0.5% and 1% and the pure zinc oxide. The 270 reduction could be attributed to the smaller ion radius of tungsten. In addition, the density of the 271 doped samples was greater compared to the undoped zinc oxide nanoparticles, so that the 2% 272 doped nanoparticles had higher molecular density compared to the other nanoparticles [48]. 273 Similar results have been reported by other researchers. For example, Siriwong et al. reported 274 that doping ZnO with WO<sub>3</sub>, the peaks intensity did not change after doping [49]. In addition, 275 slight displacement of the peaks could be differentiated in the peaks, which could be attributed to 276 the effect of WO<sub>3</sub> as dopant. They also stated that the amorphous phase of ZnO and WO<sub>3</sub> peaks 277 was not found in the XRD patterns. Because WO<sub>3</sub> concentration was too low and WO<sub>3</sub> particle 278 size was too small, therefore, it cannot affect the appearance of the peaks in the XRD patterns 279 [50]. In other words, the intensity and sharpness of all diffraction patterns have not changed, and 280

this reflects the fact that ZnO crystallinity did not change before or after doping with WO<sub>3</sub>. 281 Several methods have been proposed for the estimation of the mean size of crystals in XRD 282 patterns, the simplest of which is the Scherrer equation [51], as follows: 283

$$\tau = \frac{\kappa\lambda}{\beta\cos\theta} \tag{2}$$

where  $\tau$  is the mean size of the crystals (nm), K denotes the crystal shape factor (dimensionless), 284  $\lambda$  represents the XRD wavelength (nm) (with Cu radiation of 0.154 nm), and  $\beta$  shows the line 285

broadening at half the maximum intensity (degree to be converted into the length unit). 286

Considering the data insertion in Equation 2, the size of the 2% tungsten oxide-doped zinc oxide 287 nanoparticles was 48.25 nanometers, and the maximum intensity of the patterns was observed at 288 289 20=37.06 (101). A similar study conducted on manganese-doped zinc oxide indicated that the cell parameter increased in the doped samples, while the density decreased. Moreover, no new 290 peaks were added to the XRD pattern of the doped zinc oxide nanoparticles compared to the 291 292 pure nanoparticles in the mentioned research, while only the displacement of the peaks was reported, indicating the presence of manganese in the composition [52]. 293

Figure 6 shows a three-dimensional AFM image of 2% tungsten oxide-doped zinc oxide 294 nanoparticles at the contact and scan distance of 3×3 µm modes. In addition, the particle size 295 and nanoparticle roughness analysis have been depicted in Figure 6. Accordingly, the diameter 296 297 of the nanoparticles was 49 nanometers, which is consistent with the SEM and XRD results.





Table 2 shows the zeta potential of the undoped and tungsten oxide-doped zinc oxide 301 nanoparticles. Accordingly, the doping of the zinc oxide nanoparticles with tungsten increased 302 the zeta potential and mobility of the nanoparticles. According to the findings, the zeta potential 303 of the undoped zinc oxide nanoparticles and 2% tungsten-doped zinc oxide nanoparticles was -304 7.34 and -14.45 mV, respectively. Therefore, it seems that doping results in increasing the 305 surface charge of ZnO nanoparticles. Zeta potential is considered to be a fundamental element in 306 the recognition and control of the properties of colloidal suspensions. In general, the properties 307 of suspensions could be identified by determining the interactions of the colloids. In the current 308 309 research, DLS was used to verify the size distribution of the particles in the solutions. DLS was performed on the pure zinc oxide and 2% tungsten oxide-doped zinc oxide nanoparticles. The 310 obtained results are shown in Figure 7, which are consistent with the SEM images and AFM. 311

Table 2. Zeta potential of the synthesized nanoparticles					
Nanoparticles	Zeta Potential	Zeta Potential Model	Mobility		
	(mV)		(µ/s)/(V/cm)		
Undoped ZnO	- 11.65	Smoluchowski	- 0.91		
0.5 % WO₃ doped ZnO	- 14.88	Smoluchowski	- 1.16		
1% WO₃ doped ZnO	- 14.45	Smoluchowski	- 1.13		
2% WO₃ doped ZnO	- 7.34	Smoluchowski	- 0.57		
100 80 80 100 100 80 100 10 100 10	10 8 9 100 1000 1000	0 b 0 b 0 c 0 50 100 150 Size (nm)	200		

313

314

312

Fig. 7. DLS of the synthesized nanoparticles a) pure ZnO; b) 2 % WO<sub>3</sub> doped ZnO)

315

## 316 3.2. Effect of Dopant Percentage on the Photocatalytic Degradation Efficacy of Diazinon

317 In order to determine the effect of the weight percentage of tungsten oxide as the dopant for zinc 318 oxide, the samples containing the diazinon toxin with the concentration of 20 mg/l were exposed 319 to 30 W-UV light lamps. After 60-120 minutes, sampling was performed, followed by

centrifugation, and the residual concentration of the toxin was determined (Figure 8). As is 320 depicted in Figure 8, the doped nanoparticles had higher efficiency in the removal of diazinon 321 compared to the pure (undoped) zinc oxide nanoparticles. In addition, the percentage of 322 nanoparticle doping affected the process efficiency, so that the 2% dopant exhibited the highest 323 efficiency in diazinon removal. This superiority could be attributed to the reduction of the 324 bandgap energy of the nanoparticles, higher activation to light, and increased photocatalytic 325 activity of the doped nanoparticles. In a study in this regard, Maleki (2015) reported that 326 increasing the concentration of copper as the dopant in the zinc oxide lattice enhanced its 327 photocatalytic activity [16]. Moreover, Khataei (2015) demonstrated that zinc oxide doping was 328 associated with the reduction of the bandgap energy, as well as a gradual increase in 329 photocatalytic activity [53]. 330

331



Fig.8. Effect of different dopant percentage on the photodegradation efficiency of Diazinon 333 (diazinon concentration = 20 mg/l, pH = 7, concentration of nanoparticle = 3%, UV intensity = 334 30 W) 335

336

332

337

#### 3.3. Effect of pH on the Photodegradation Efficiency of Diazinon

Figure 9 shows the results of the present study regarding the effect of the solution pH on the 338 photocatalytic degradation efficiency of 2% tungsten-doped zinc oxide. Accordingly, the 339 efficiency of toxin degradation was higher in relatively acidic environments compared to neutral 340 and alkaline environments, which could be due to the effect of pH on the dominant electrical 341 charge variation in the surface of the zinc oxide nanoparticles. It is notable that pH is an 342

#### Journal Pre-proof

important influential factor in the removal efficiency of pollutants due to its impact on the 343 pollutant ionization state and surface properties of the nanoparticles in the solution [54]. 344 Nevertheless, the isoelectric pH obtained in the previous studies in this regard have indicated that 345 in acidic environments, the surface of zinc oxide is positively charged, resulting in the higher 346 adsorption of negative-charge pollutants. Since hydroxyl free radical production is caused 347 through the induction of the surface of zinc oxide, higher pollutant adsorption at the surface 348 affects the pollutant molecules more rapidly, thereby leading to their damage and destruction 349 [55]. This condition can be explained by electrostatic interaction between the WO<sub>3</sub> doped ZnO 350 surface and diazinon. The pHzpc of ZnO is reported around 9 and thus the surface of ZnO is 351 positive below pH 9.0 [14]. In this study, the pH<sub>zpc</sub> of WO<sub>3</sub>-doped ZnO was about 8.4. Therefore, 352 the surface of the synthetized photocatalysts is positively charged at a low pH (<pH<sub>zpc</sub>), and 353 negatively charged at a higher pH (>  $pH_{zpc}$ ). On the other hand, the pKa value for diazinon is 2.6 354 and it will be negatively charged above pH 2.6. Therefore, the optimal condition for removal of 355 diazinon was occurred at  $pK_a^{Diazinon} < pH < pH_{zpc}^{W03-doped ZnO}$  (between 2.6 < pH < 8.4) at 356 357 which the positively charged WO<sub>3</sub> -doped ZnO and negatively charged diazinon molecules easily and quickly absorb each other and ultimately, it increases the photodegradation of diazinon. 358 Based on the results, pH 7 was determined as an optimum condition for the degradation of 359 diazinon using WO<sub>3</sub>-doped ZnO nanoparticle. It should be noted that the main reason for the 360 highest percentage of diazinon degradation in pH 7 is due to photo-corrosion of ZnO in acidic 361 and basic solutions [56]. 362

363



369

Fig. 9. Effect of pH on the photodegradation efficiency of diazinon using 2% WO<sub>3</sub> doped ZnO
nanoparticles (diazinon concentration = 20 mg/l, nanoparticle suspension concentration = 3%,
light intensity = 30 W)

370 3.4.Effect of Nanoparticle Dosage on Diazinon Photodegradation Efficiency

Figure 10 depicts the findings of the current research regarding the effect of various dosages of 2% tungsten oxide-doped zinc oxide nanoparticles on its photocatalytic properties. As is evident, the increased dosage of the nanoparticles from 2 to 10 mg/cm<sup>2</sup> was associated with the higher efficiency of the process at a slight gradient, so that at the contact time of 60 minutes, degradation efficiency was recorded within the range of 70.5-80%.

One of the most important issues in this system is determining the amount of the catalyst due to economic considerations. Increasing the dosage of the catalyst could results in the higher efficiency of the photocatalytic process through making the surface more accessible to absorption, thereby increasing the contact between the pollutant and catalyst [57]. In a research in this regard, Ba-Abbad et al. (2010) reported that nanocatalysts increased the process efficiency to a certain value, while this was follows by the reduced decomposition efficiency through causing turbidity in the solution and diminishing light penetration [58, 59].



Fig. 10. Effect of 2% WO<sub>3</sub> doped ZnO dosage on the photodegradation efficiency of diazinon
(Diazinon concentration = 20 mg/l, nanoparticle suspension concentration =3%, light intensity = 30 W)

389 390

391

## 3.5. Effect of the Initial Concentration of Diazinon on Its Photodegradation Efficiency

Figure 11 shows the results of the present study regarding the effects of various concentrations of 392 diazinon on its photocatalytic degradation using 2% tungsten oxide-doped zinc oxide 393 nanoparticles. As can be seen, the increased initial concentration of diazinon was associated with 394 395 decreased degradation efficiency, so that after 60 minutes, increasing the concentration of diazinon from 10 to 200 mg/l caused the removal efficiency to decrease from 88.6% to 44.4%. 396 This could be due to the fact that the higher concentration of diazinon causes more active surface 397 catalyst sites to be covered, which in turn reduces the production of oxidizing radicals and 398 ultimately the decomposition rate. In addition, high concentrations of pollutants absorb more 399 400 photons from ultraviolet radiation, thereby decreasing the flux of ultraviolet photons for catalytic activation. Meanwhile, the lack of active surface catalyst sites reduces oxidative production, as 401 well as the decomposition rate of toxins. Several studies regarding the treatment of various 402 pollutants through the photocatalytic processes of zinc oxide have indicated that degradation 403 efficiency decreases with the increased initial concentration of the pollutant [60-63]. 404



Fig. 11. Effect of initial concentration of diazinon on its photodegradation efficiency using 2%
 WO<sub>3</sub> doped ZnO nanoparticles (nanoparticles suspension concentration = 3%, light intensity = 30 W)

#### 415 3.6.Effect of the Contact Time on the Photodegradation Efficiency of Diazinon

Figure 12 shows the results of the present study regarding the effect of the contact time on the photocatalytic degradation of diazinon using 2% tungsten oxide-doped zinc oxide nanoparticles. Accordingly, the efficiency of diazinon degradation increased with a relatively linear, steep slope within 10-30 minutes, while the efficiency partially increased within 30-180 minutes, particularly at 45-120 minutes, when the process efficiency was almost unmatched. Therefore, it could be concluded that at the outset of the process, the available catalyst surfaces are completely free, and as a result, the entire catalyst surface is at the disposal of the diazinon, resulting in the removal efficiency with a steep increase; however, available surfaces and degradation efficiency decrease over time. 



Fig. 12. Effect of contact time on the photodegradation efficiency of diazinon using 2% WO<sub>3</sub>
doped ZnO nanoparticles (Diazinon concentration = 20 mg/l, nanoparticle suspension
concentration = 3%, light intensity = 30 W)

# 431 3.7. Effects of Light Intensity and Source and Nanoparticle Dispersion on the 432 Photodegradation of Diazinon

In order to investigate the effects of ultraviolet light on the photocatalytic degradation of 433 diazinon, specimens containing 20 mg/l of diazinon were prepared and exposed to ultraviolet 434 light with the intensities of 6, 18, and 30 Watts. According to the obtained results, the increasing 435 of the ultraviolet light was associated with significantly higher degradation efficiency. After 60 436 minutes, the increasing of light intensity from 6 to 30 Watts caused the damage removal 437 efficiency to increase from 22% to 83% (Figure 13a). This could be attributed to the increased 438 radiation in the zinc oxide nanoparticles that were immobilized on the glass; as such, the 439 increased intensity of ultraviolet radiation led to the increased excitation of the electrons, as well 440 as the degradation efficiency. Similar findings have been proposed in the literature in this regard 441 [64]. For instance, Kamat et al. reported that the removal efficiency of 4-chlorocatechol 442 increased at the higher intensity and duration of irradiation [65]. To assess the effect of radiation 443 source on the process efficiency, we investigated the rate of diazinon degradation in the presence 444 of light (visible and ultraviolet) and absence of light with slurry and immobilized nanoparticles 445 placed on the glass. As is depicted in Figure 12b, ultraviolet light exhibited higher efficacy in 60 446 minutes compared to visible light, so that the efficiency of the former was approximately 18% 447

higher than the latter in diazinon degradation. However, at the contact time of 120 minutes, the 448 difference in this regard reduced, and the efficiency of both light sources only had a slight 449 difference, in which case almost 83 and 87% of the destruction occurred (Figure 13b). Another 450 451 notable point is the method of using the nanoparticles. In the case of slurry nanoparticles, degradation efficiency was significantly lower compared to the immobilized nanoparticles 452 (Figure 13c). Therefore, the immobilization of the nanoparticles reduced the application of the 453 nanoparticles, thereby preventing its release into the environment. In order to evaluate the effect 454 of different processes on the photocatalytic degradation of diazinon by using different 455 photocatalysts, the results of this study was compared with other reported data and summarized 456 in Table 3. This comparison shows that the WO<sub>3</sub>-doped ZnO is an effective photocatalyst for the 457 degradation of diazinon compared to other photocatalysts. 458

- 459
- 460
- 461

Table 3. Con	parison of phot	ocatalytic degrae	dation of diazinon.
--------------	-----------------	-------------------	---------------------

Photocatalyst	dosage	Light source	Time (min)	Concentration (mg/l)	<mark>pH</mark>	Removal (%)	Reference
Fe-TiO <sub>2</sub> /Bent- Fe	<mark>0.5 g/l</mark>	visible light (36 W compact bulb)	-	<mark>25</mark>	<mark>5.6</mark>	<mark>58.3</mark>	<mark>[66]</mark>
WO <sub>3</sub>	0.5 g/l	UV light (125- W medium- pressure UVC lamp)	<mark>120</mark>	20	<mark>3</mark>	<mark>99.88</mark>	[31]
Fe-TiO₂	<mark>0.1 g/l</mark>	UV light (125- W medium- pressure UVC lamp)	<mark>60</mark>	<mark>50</mark>	7	<mark>98.53</mark>	[13]
<mark>MgO</mark>	<mark>0.1 g/l</mark>	<mark>UV light</mark> (5 lamps)	<mark>120</mark>	<mark>5</mark>	7	<mark>99.46</mark>	<mark>[67]</mark>
Iron doped TiO <sub>2</sub>	<mark>0.4 g/l</mark>	UV light (15-W low pressure UV lamp)	<mark>100</mark>	<mark>30</mark>	<mark>5.5</mark>	<mark>76</mark>	[68]
<mark>FeFNS-doped</mark> TiO <sub>2</sub>	<mark>0.25 g/l</mark>	<mark>UV-LEDs</mark>	<mark>100</mark>	<mark>1.3</mark>	<mark>7</mark>	<mark>44.8</mark>	<mark>[12]</mark>
Fe <sub>3</sub> O <sub>4</sub> /HAP	<mark>4 g/l</mark>	UV light (30 W low- pressure lamp)	<mark>60</mark>	10	<mark>5.5</mark>	<mark>75</mark>	<mark>[69]</mark>
WO <sub>3</sub> -doped ZnO	10 mg/cm <sup>2</sup>	UV light (five (6 W) low- pressure lamp)	<mark>120</mark>	20	7	<mark>89</mark>	<mark>This</mark> study
WO <sub>3</sub> -doped ZnO	10 mg/cm <sup>2</sup>	<mark>Sunlight</mark>	<mark>120</mark>	<mark>20</mark>	7	<mark>83</mark>	<mark>This</mark> study



Fig. 13. Effect of (a) light intensity, (b) light source for immobilized and (c) light source for slurry 2% WO<sub>3</sub> doped ZnO nanoparticles on the photodegradation efficiency of diazinon (Diazinon concentration = 20 mg/l, nanoparticle suspension concentration = 3%)

#### 472 **3.8. Kinetic Study and Electrical Energy Determination**

The kinetics of the photocatalytic decomposition of many organic pollutants is described by pseudo-first order kinetics and the rate expression is given by Eq. (3). [70]:

$$Ln\frac{C_0}{C} = k_{obs}t \qquad (3)$$

where  $k_{obs}$  (1/min) is the pseudo-first order rate constant, C and C<sub>0</sub> are the concentration at time t' and 't=0', respectively. Plotting  $ln(C_0/C)$  versus time base on equation 3 is presented in Figure 14a and K<sub>obs</sub> (equation 3), according to calculating slope and intercept of the line.

In this study, the kinetics of diazinon degradation was examined for at optimum conditions 478 according to the first order model and its results are presented in Table 4. As can be seen from 479 the table, k<sub>obs</sub> decreases as the initial diazinon concentration increases. This is due to the decrease 480 in the number of active sites on the catalyst surface due to its surface being coated with diazinon 481 molecules, which ultimately reduces the rate of production of oxidizing radicals and holes [14]. 482 483 However, in most previous studies the relationship between the initial photocatalytic degradation rate and the initial concentration of organic substrate for a heterogeneous photocatalytic process 484 has been analyzed with the Langmuir-Hinshelwood (L-H) model [14, 71, 72]. This model 485 considers that the rate of oxidation of substrate at surface reaction is proportional to the surface 486 coverage of diazinon on the WO<sub>3</sub> doped ZnO photocatalyst assuming that substrate is adsorbed 487 on the catalyst surface than the intermediate products [14]. Eqs. (4) and (5) are used to describe 488 this model [14]: 489

490

$$r = \frac{k_c K_{L-H}(C)}{1 + K_{L-H}(C_0)} = k_{obs}(C)$$
(4)  
$$\frac{1}{k_{obs}} = \frac{1}{k_c K_{L-H}} + \frac{C_0}{k_c}$$
(5)

491 where  $C_0$  is the initial concentration of diazinon (mg L<sup>-1</sup>),  $k_c$  (mg L<sup>-1</sup> min<sup>-1</sup>) is the kinetic rate 492 constant of surface reaction and  $K_{L-H}$  (L/mg) is the Langmuir adsorption constant. The values of 493 kc and  $K_{L-H}$  were obtained as 0.67 (mg L<sup>-1</sup> min<sup>-1</sup>) and 0.023 (L/mg), respectively, for the 494 photodegradation of diazinon using 2% WO<sub>3</sub> doped ZnO. This L–H kinetic model has been used 495 by several authors to analyze heterogeneous photocatalytic reactions (Figure 14b). According to 496 Daneshvar *et al.* the values of  $K_{L-H}$  and kc for degradation of diazinon by UV/ZnO were 0.124 497 L/mg and 0.209 mg L<sup>-1</sup> min<sup>-1</sup>, respectively [14].





Fig. 14. (a) The plots of  $ln(C_0/C)$  versus irradiation time at different initial diazinon concentrations and (b) the plot of  $1/k_{obs}$  versus different diazinon concertation for different as prepared WO<sub>3</sub> doped ZnO nanoparticles (Diazinon concentration = 10 mg/l, nanoparticle suspension concentration =3%, light intensity = 30 W, and pH=7)

503	Table 4. Pseudo-first order kinetics (k <sub>obs</sub> ), half-life times and E <sub>EO</sub> values for diazinon degradation
504	using 2% WO <sub>3</sub> doped ZnO nanoparticles at different initial concentrations

Concentration (mg/L)	K <sub>obs</sub> (min ⁻¹)	t <sub>1/2</sub> (min)	<mark>r²</mark>	E <sub>EO</sub> (kWh/m³)
<mark>10</mark>	<mark>0.0205</mark>	<mark>33.8</mark>	<mark>0.98</mark>	<mark>112.4</mark>
<mark>20</mark>	<mark>0.0098</mark>	<mark>70.7</mark>	<mark>0.99</mark>	<mark>235</mark>
<mark>50</mark>	<mark>0.0068</mark>	<mark>102</mark>	<mark>0.99</mark>	<mark>339</mark>
<mark>100</mark>	<mark>0.0042</mark>	<mark>165</mark>	<mark>0.95</mark>	<mark>548</mark>
<mark>200</mark>	<mark>0.0034</mark>	<mark>204</mark>	<mark>0.93</mark>	<mark>677</mark>

There are different parameters such as economics, economy of scale, regulations, effluent quality 506 goals, operation (maintenance, control, safety) to evaluate a wastewater treatment method and 507 finally to select a suitable method [71, 72]. Since economics is recognized as the most important 508 509 factor, process optimization is important in order to minimize the cost of operating wastewater 510 treatment processes in Advanced Oxidation Technologies (AOTs) because photocatalysis is an electric energy intensive process and electrical energy is responsible for many operating costs 511 [42, 73]. For this reason, the evaluation of electrical energy is necessary and should be provided, 512 especially for the real application [71]. Accordingly, a figure-of-merit (FOM) of the process 513 based on electric energy consumption is useful and informative. Recently, the Photochemistry 514 515 Commission of the International Union of Pure and Applied Chemistry (IUPAC) introduced two figures-of-merit (for low and high concentration of pollutants) to evaluate UV-based AOTs 516

based on electrical energy [42, 73]. The suitable figure of merit in the case of low pollutant concentration is the electrical energy per order ( $E_{EO}$ ). It is defined as the number of kWh of electrical energy required to reduce the concentration of a contaminant by one order of magnitude (90%) in 1000 L of contaminated water [73]. The  $E_{EO}$  (kWh/m<sup>3</sup>/order) can be calculated from the following equations (Eq 6) for a batch type reactor [42]:

$$E_{EO} = \frac{P \times t \times 1000}{V \times 60 \times \log C_0 / C}$$
(6)

where P is the lamp power (kW), V is the treated volume (L) of water in the reactor, Co and C are the initial and final concentrations of pollutant and t is the time of irradiation (min). This equation for a pseudo-first-order reaction in a batch reactor can be written as follows (Eq 7) [42]:

$$E_{EO} = \frac{38.4 \times P}{V \times K_{obs}} \tag{7}$$

525

where  $k_{obs}$  is the pseudo-first-order reaction rate constant (min<sup>-1</sup>). The E<sub>EO</sub> values for 526 photocatalytic degradation of diazinon in the presence of synthesized nanocatalysts have been 527 given in Table 5. These results show that the  $E_{EO}$  values for degradation of 10 mg/L diazinon by 528 2% WO<sub>3</sub> doped ZnO, 1% WO<sub>3</sub> doped ZnO, 0.5% WO<sub>3</sub> doped ZnO and pure ZnO catalysts were 529 112, 166, 562 and 242 kWh/m<sup>3</sup>, respectively and the photocatalysis process in presence of 2% 530 WO<sub>3</sub> doped ZnO offered the best energy efficiency. The E<sub>EO</sub> value for 2% WO<sub>3</sub> doped ZnO 531 photocatalyst was lower than other photocatalysts and E<sub>EO</sub> amount for the photodegradation of 532 diazinon in the presence of 2% WO<sub>3</sub> doped ZnO is 5 times more than 0.5% WO<sub>3</sub> doped ZnO. 533 Therefore, the  $E_{EO}$  decreases with increasing  $k_{obs}$ . Daneshvar et al. reported  $E_{EO}$  values of 20000, 534 1388.8 and 1075.3 kWh/m<sup>3</sup> for photodegradation of diazinon (20 mg/L) by photolysis, UV/ZnO 535 (33nm) and UV/ZnO (14nm) processes, respectively [14]. These results also show that the 536 electrical energy consumption is directly proportional to the photocatalytic activity of the 537 photocatalyst. In fact, 2% WO<sub>3</sub> doped ZnO photocatalyst with high activity needs less energy 538 consumption in comparison to other synthesised photocatalyst [72]. The higher electrical energy 539 consumption means lower process efficiency [74]. So the E<sub>EO</sub> can be considered as an important 540 541 factor in assessing the treatment costs [72].

542

Table 5. Langmuir-Hinshelwood (L-H) model kinetics (k<sub>c</sub> and K<sub>L-H</sub>) and E<sub>EO</sub> values for 544 photocatalytic degradation of diazinon using different as prepared WO<sub>3</sub> doped ZnO (Diazinon 545 concentration = 10 mg/l, nanoparticle suspension concentration = 3%, light intensity = 30 W, and 546 pH=7) 547

<mark>Catalyst</mark>	k <sub>c</sub> (mg L⁻¹ min⁻¹)	<mark>К<sub>L-Н</sub> (L/mg)</mark>	r <sup>2</sup>	<mark>E<sub>EO</sub> (kWh/m³)</mark>
<mark>2%WO₃ doped ZnO</mark>	<mark>0.67</mark>	<mark>0.023</mark>	<mark>0.97</mark>	<mark>112</mark>
<mark>1%WO₃ doped ZnO</mark>	<mark>0.82</mark>	<mark>0.0158</mark>	<mark>0.96</mark>	<mark>166</mark>
<mark>0.5%WO₃ doped ZnO</mark>	<mark>0.391</mark>	<mark>0.0084</mark>	<mark>0.93</mark>	<mark>562</mark>
<mark>Pure ZnO</mark>	<mark>0.844</mark>	<mark>0.0103</mark>	<mark>0.92</mark>	<mark>242</mark>

548

#### 3.9. Optical absorption and UV-Vis spectra 549

UV-Vis spectroscopy is an efficient way to determine the ability of a semiconductor to absorb 550 light at different wavelengths. Figure 15 shows the results of the UV-Vis spectra of different 551 synthesized nanoparticles. The results showed that the optical absorption band of pure ZnO is in 552 380 nm with band gap of 3.25 eV. Thus pure ZnO absorbs up to 380 nm of light and has no 553 absorption in the visible light range. But after doping with WO<sub>3</sub>, the range of light absorption 554 shifts to longer wavelengths. This is attributed to the formation of the energy level of vacancy 555 oxygen, since the WO<sub>3</sub> contained in the zinc oxide crystal lattice can cause the formation a 556 557 vacancy oxygen [75]. According to the results, the optical absorption band of 0.5% WO<sub>3</sub>-doped ZnO, 1% WO<sub>3</sub>-doped ZnO and 2% WO<sub>3</sub>-doped ZnO is 439 (2.81 eV), 440 (2.8 eV), and 441 558 (2.80 eV), respectively. Thus, compared to pure ZnO, the absorption edge of the WO<sub>3</sub>-doped 559 560 ZnO nanoparticles shows red shift. Similar results have been reported for the effect of dopant on the absorption edge change by Xie et al. [76]. 561



564 Fig 15. UV–Vis absorbance spectra of pure ZnO and WO<sub>3</sub>-doped ZnO nanoparticles

#### 565 Conclusion

The present study aimed to evaluate the efficiency of the photocatalytic degradation of diazinon 566 in aqueous media using tungsten-doped zinc oxide nanoparticles. According to the obtained 567 results, the addition of tungsten oxide to the zinc oxide nanoparticles reduced the network 568 constant and increased its density, which in turn improved its efficacy in the photocatalytic 569 570 process. Furthermore, the findings indicated that the increased nanoparticle size distribution, nanoparticle dosage, light intensity, and contact time were associated with the higher efficiency 571 of the photocatalytic process in diazinon degradation and vice versa. On the other hand, the 572 573 increased pH of the environment and initial concentration of diazinon were observed to decrease the degradation process efficiency. Therefore, it could be concluded that the process of 574 575 photocatalytic degradation using tungsten-doped zinc oxide nanoparticles could positively affect the removal of organic pollutants, including diazinon, from aqueous media. In addition, 576 the surface immobilization of the nanoparticles reduced their consumption, thereby preventing 577 their release into the environment. 578

579

#### 580 Acknowledgement

Research reported in this publication was supported by Elite Researcher Grant Committee under
award number [963307] from the National Institutes for Medical Research Development
(NIMAD), Tehran, Iran

#### 584 **References**

- 585 [1] M.F. Abid, S.K. Al-Naseri, Q.F. Al-Sallehy, S.N. Abdulla, K.T. Rashid, Desalination and Water Treatment 586 29 (2011) 174.
- 587 [2] P. Mahmoodi, H. Hosseinzadeh Borazjani, M. Farhadian, A. Solaimany Nazar, Desalination and water 588 treatment 53 (2015) 2948.
- 589 [3] A.A. Shipp, Water-quality Assessment in the Trinity River Basin, Texas: Pesticide Occurrence in 590 Streams, Winter and Spring 1994. US Geological Survey, 1995.
- 591 [4] A. Jonidi-Jafari, M. Shirzad-Siboni, J.-K. Yang, M. Naimi-Joubani, M. Farrokhi, Journal of the Taiwan 592 Institute of Chemical Engineers 50 (2015) 100.
- 593 [5] J. Fenoll, P. Hellín, P. Flores, C.M. Martínez, S. Navarro, Chemosphere 87 (2012) 954.
- [6] J. Abraham, S. Silambarasan, P. Logeswari, Journal of the Taiwan Institute of Chemical Engineers 45(2014) 2590.
- 596 [7] D. Wang, N. Singhasemanon, K.S. Goh, Environmental monitoring and assessment 189 (2017) 310.
- 597 [8] Y. Zhang, Y. Hou, F. Chen, Z. Xiao, J. Zhang, X. Hu, Chemosphere 82 (2011) 1109.
- 598 [9] A. Jonidi-Jafari, M. Gholami, M. Farzadkia, A. Esrafili, M. Shirzad-Siboni, Separation Science and 599 Technology 52 (2017) 2395.
- 600 [10] A. Naeimi Bagheini, M. Saeidi, N. Boroomand, International Journal of Nanoscience and 601 Nanotechnology 14 (2018) 19.
- [11] L. Kazemizad, Y. Ghaffari, M. Kermani, M. Farzadkia, A. Hajizadeh, Journal of Safety, Environment,
  and Health Research 1 (2016) 17.
- 604 [12] H. Hossaini, G. Moussavi, M. Farrokhi, Water research 59 (2014) 130.
- [13] M.M. Baneshi, S. Rezaei, A. Sadat, A. Mousavizadeh, M. Barafrashtehpour, H. Hekmatmanesh,
   Bioscience Biotechnology Research Communication (2017) 60.
- [14] N. Daneshvar, S. Aber, M.S. Dorraji, A. Khataee, M. Rasoulifard, International Journal of Nuclear and
   Quantum Engineering 1 (2007) 62.
- [15] R.-S. Juang, C.-H. Chen, Journal of the Taiwan Institute of Chemical Engineers 45 (2014) 989.
- [16] A. Maleki, M. Safari, B. Shahmoradi, Y. Zandsalimi, H. Daraei, F. Gharibi, Environmental Science and
  Pollution Research 22 (2015) 16875.
- [17] A. Maleki, A. Mahvi, M. Alimohamadi, A. Ghasri, Pakistan Journal of Biological Sciences 9 (2006)2338.
- [18] R. Rezaee, A. Maleki, A. Jafari, S. Mazloomi, Y. Zandsalimi, A.H. Mahvi, Journal of Environmental
  Health Science and Engineering 12 (2014) 67.
- 616 [19] A.K.L. Sajjad, S. Sajjad, A. Iqbal, Ceramics International (2018).
- 617 [20] A. Maleki, B. Shahmoradi, Water Science and Technology 65 (2012) 1923.
- 618 [21] B. Shahmoradi, A. Maleki, K. Byrappa, Desalination and Water Treatment 53 (2015) 3615.
- [22] M. Elias, M.K. Amin, S.H. Firoz, M.A. Hossain, S. Akter, M.A. Hossain, M.N. Uddin, I.A. Siddiquey,
  Ceramics International 43 (2017) 84.
- 621 [23] B. Shahmoradi, K. Soga, S. Ananda, R. Somashekar, K. Byrappa, Nanoscale 2 (2010) 1160.
- 622 [24] C. Xu, L. Cao, G. Su, W. Liu, X. Qu, Y. Yu, Journal of Alloys and Compounds 497 (2010) 373.
- 623 [25] H. Tada, A. Kokubu, M. Iwasaki, S. Ito, Langmuir 20 (2004) 4665.
- [26] H.F. Moafi, M.A. Zanjanchi, A.F. Shojaie, Materials Chemistry and Physics 139 (2013) 856.
- 625 [27] M.S. Dresselhaus, G. Dresselhaus, R. Saito, A. Jorio, Physics reports 409 (2005) 47.
- [28] A. Senthilraja, B. Subash, B. Krishnakumar, D. Rajamanickam, M. Swaminathan, M. Shanthi,
   Materials Science in Semiconductor Processing 22 (2014) 83.
- 628 [29] A.K.L. Sajjad, S. Shamaila, B. Tian, F. Chen, J. Zhang, Journal of Hazardous materials 177 (2010) 781.
- 629 [30] T. Ohno, F. Tanigawa, K. Fujihara, S. Izumi, M. Matsumura, Journal of Photochemistry and
- 630 Photobiology A: Chemistry 118 (1998) 41.

- [31] A. Mohagheghian, K. Ayagh, K. Godini, M. Shirzad-Siboni, Journal of Advanced Oxidation
   Technologies 20 (2017).
- 633 [32] H. Wang, P. Xu, T. Wang, Materials & design 23 (2002) 331.
- [33] S. Singh, V.C. Srivastava, S.L. Lo, Materials Science Forum, Trans Tech Publ, 2016, p. 105-126.
- [34] A. Hammad, H.M. El-Bery, A. EL-Shazly, M. Elkady, Int. J. Electrochem. Sci 13 (2018) 362.
- [35] N. Ramos-Delgado, M. Gracia-Pinilla, L. Maya-Trevino, L. Hinojosa-Reyes, J. Guzman-Mar, A.
  Hernández-Ramírez, Journal of hazardous materials 263 (2013) 36.
- [36] N. Ramos-Delgado, L. Hinojosa-Reyes, I. Guzman-Mar, M. Gracia-Pinilla, A. Hernández-Ramírez,
  Catalysis Today 209 (2013) 35.
- [37] C. Rajan, International journal of Environmental science and Development 2 (2011) 182.
- [38] M. Pirsaheb, B. Shahmoradi, M. Beikmohammadi, E. Azizi, H. Hossini, G.M. Ashraf, Scientific reports
  7 (2017) 1473.
- [39] B. Shahmoradi, K. Namratha, K. Byrappa, K. Soga, S. Ananda, R. Somashekar, Research on Chemical
  Intermediates 37 (2011) 329.
- [40] M. Behnajady, N. Modirshahla, N. Daneshvar, M. Rabbani, Chemical Engineering Journal 127 (2007)167.
- [41] M.A. Behnajady, N. Modirshahla, M. Mirzamohammady, B. Vahid, B. Behnajady, Journal of
  hazardous materials 160 (2008) 508.
- [42] J. Carneiro, A. Samantilleke, P. Parpot, F. Fernandes, M. Pastor, A. Correia, E. Luís, A. Chivanga
  Barros, V. Teixeira, Journal of Nanomaterials 2016 (2016) 21.
- [43] Y.J. Kwon, K.H. Kim, C.S. Lim, K.B. Shim, Journal of ceramic processing research 3 (2002) 146.
- 652 [44] V.D. Mote, V.R. Huse, B.N. Dole, (2012).
- 653 [45] V.B. Kumar, D. Mohanta, Bulletin of Materials Science 34 (2011) 435.
- [46] J. Díaz-Reyes, V. Dorantes-García, A. Pérez-Benítez, J. Balderas-López, Superficies y vacío 21 (2008)
  12.
- 656 [47] H. Sowa, H. Ahsbahs, Journal of applied crystallography 39 (2006) 169.
- [48] P. Kathirvel, D. Manoharan, S. Mohan, S. Kumar, J Optoelectron Biomed Mater 1 (2009) 25.
- [49] C. Siriwong, K. Wetchakun, A. Wisitsoraat, S. Phanichphant, Sensors, 2009 IEEE, IEEE, 2009, p. 118123.
- 660 [50] C. Siriwong, S. Phanichphant, Chiang Mai J. Sci 40 (2013) 281.
- 661 [51] C. Zimmer, S. Wright, R. Engelhardt, G. Johnson, C. Kramm, X. Breakefield, R. Weissleder, 662 Experimental neurology 143 (1997) 61.
- [52] O. Jayakumar, I. Gopalakrishnan, R. Kadam, A. Vinu, A. Asthana, A. Tyagi, Journal of Crystal Growth300 (2007) 358.
- [53] A. Khataee, R.D.C. Soltani, A. Karimi, S.W. Joo, Ultrasonics sonochemistry 23 (2015) 219.
- [54] M. Hadi, G. McKay, M.R. Samarghandi, A. Maleki, M. Solaimany Aminabad, Desalination and Water
   Treatment 49 (2012) 81.
- 668 [55] C.-H. Wu, Dyes and Pigments 77 (2008) 31.
- [56] M. Shirzad-Siboni, A. Jonidi-Jafari, M. Farzadkia, A. Esrafili, M. Gholami, Journal of environmental
   management 186 (2017) 1.
- [57] Z. Noorimotlagh, R.D.C. Soltani, A. Khataee, S. Shahriyar, H. Nourmoradi, Journal of the Taiwan
  Institute of Chemical Engineers 45 (2014) 1783.
- [58] M. Tabatabaee, S. Abolfazl Mirrahimi, Oriental Journal of Chemistry 27 (2011) 65.
- [59] M. Ghaneian, M. Salmani, M. Ehrampoush, A. Dehghani, M. Nafisl, Tolooebehdasht 14 (2016) 227.
- [60] S. Pardeshi, A. Patil, Journal of Molecular Catalysis A: Chemical 308 (2009) 32.
- [61] A.M. Rahman, M. Qamar, M. Muneer, D. Bahnemann, Journal of Advanced Oxidation Technologies9 (2006) 103.
- [62] K. Parida, S. Dash, D. Das, Journal of colloid and interface science 298 (2006) 787.

- 679 [63] M. Qamar, M. Muneer, Desalination 249 (2009) 535.
- [64] I. Carra, J.A. Sánchez Pérez, S. Malato, O. Autin, B. Jefferson, P. Jarvis, Journal of Chemical
  Technology and Biotechnology 91 (2016) 72.
- [65] P. Kamat, R. Huehn, R. Nicolaescu, Abstracts of Papers of the American Chemical Society, AMER
  CHEMICAL SOC 1155 16TH ST, NW, WASHINGTON, DC 20036 USA, 2002, p. U519-U519.
- [66] N.M. Phuong, N.C. Chu, D. Van Thuan, M.N. Ha, N.T. Hanh, H.D.T. Viet, M. Thu, N. Thi, P. Van Quan,
  T. Truc, Journal of Chemistry 2019 (2019).
- 686 [67] T. Ahmadifard, R. Heydari, M.J. Tarrahi, G.S. Khorramabadi, International Journal of Chemical 687 Reactor Engineering (2019).
- 688 [68] S. Tabasideh, A. Maleki, B. Shahmoradi, E. Ghahremani, G. McKay, Separation and Purification 689 Technology 189 (2017) 186.
- 690 [69] Z.-p. Yang, X.-y. Gong, C.-j. Zhang, Chemical Engineering Journal 165 (2010) 117.
- [70] M. Ahmadi, P. Amiri, Journal of Applied Research in Water and Wastewater 3 (2016) 271.
- 692 [71] A. Mohagheghian, S.-A. Karimi, J.-K. Yang, M. Shirzad-Siboni, Journal of Advanced Oxidation
- 693 Technologies 18 (2015) 61.
- [72] R. Mohammadi, B. Massoumi, H. Eskandarloo, Desalination and Water Treatment 53 (2015) 1995.
- [73] A. Khataee, H. Aleboyeh, A. Aleboyeh, Journal of Experimental Nanoscience 4 (2009) 121.
- [74] S. Khezrianjoo, H.D. Revanasiddappa, Water Quality Research Journal 51 (2016) 69.
- [75] Y. Changlin, Y. Kai, S. Qing, C.Y. Jimmy, C. Fangfang, L. Xin, Chinese Journal of Catalysis 32 (2011)555.
- [76] J. Xie, Z. Zhou, Y. Lian, Y. Hao, X. Liu, M. Li, Y. Wei, Ceramics International 40 (2014) 12519.



Fig. 3. EDS spectra of (a) pure ZnO and (b)  $%WO_3$  doped ZnO.

Johngible

## Highlights

- WO<sub>3</sub> doped ZnO NPs was used for photocatalytic degradation of diazinon under UV light irradiation.
- Photocatalytic activity of ZnO NPs was improved after doping with tungsten oxide.
- The photocatalysis process in presence of 2% WO<sub>3</sub> doped ZnO offered the best energy efficiency
- The stabilization of the nanoparticle was done to reduce the amount of nanocatalysts consumption and its release rate.

Jonulaible

October 9, 2019

## **Conflict of Interest**

All authors agree to submit the revised manuscript entitled "**The photocatalytic** removal of diazinon from aqueous solutions using tungsten oxide doped zinc oxide nanoparticles immobilized on glass substrate" for consideration to publish in the *J* of

Molecular Liquids.

With best regards,

Seung-Mok Lee, Professor Department of Environmental Engineering Catholic Kwandong University, Gangneung 25601, R. of Korea