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Photocatalytic degradation of diazinon by illuminated WO_3 nanopowder

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ABSTRACT

In this study, photocatalytic degradation of diazinon as a model phosphorothioate insecticide by tungsten oxide nanopowder under UV irradiation was investigated. Effect of operational parameters including WO_3 dosage, pH, initial diazinon concentration, and organic compounds (humic acid, oxalic acid, phenol, ethylenediaminetetraacetic acid (EDTA)) on the photocatalytic degradation of diazinon was studied. Degradation efficiency of diazinon by WO_3/UV process was more effective than WO_3-alone and UV-alone. As the nanocatalyst dosage increased, the photocatalytic degradation of the diazinon decreased. Removal efficiency was decreased by increasing pH and initial diazinon concentration. The reaction rate constant (k_{obs}) was decreased from 0.1233 to 0.0001/min, and the value of electrical energy per order (E_{Eo}) was increased from 38.93 to 48,000 (kWh/m^3) with increasing initial diazinon concentration from 5 to 50 mg/L, respectively. The photocatalytic degradation of diazinon was increased in the presence of oxalic acid and EDTA, while different trend was observed in the presence of phenol and humic acid. Proper photocatalytic activity was observed even after five successive cycles. Finally, UV/WO_3 is identified as a promising technique for the removal of diazinon with high efficiency in a short reaction time.

Keywords: Tungsten oxide; Diazinon; Photocatalysis; Kinetics

1. Introduction

Several insecticides are commonly found in aquatic system due to several activities such as chemical spills, industrial effluents, and agricultural runoffs. Most insecticides have persistence, stability, and toxicity, which cause much concern in regulation and protection of them from environments [1]. Diazinon (O,O-Diethyl O-[4-methyl-6-(propan-2-yl)pyrimidin-2-yl] phosphorothioate) is one kind of organophosphorus insecticides and is categorized as moderately hazardous of class II by the World Health Organization (WHO) [2,3]. Vapor pressure of diazinon is known as 1.4×10^{-4} mmHg at 20°C, which indicates that it is persistent and stable in water and soil [4,5]. Lethal concentration (LC_{50}) of the diazinon for aquatic organisms is equal to 350 ng/L [1,5]. Toxic effect of the diazinon on human body is related to its inhibition of the

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enzyme acetylcholinesterase [6]. Therefore, surface and groundwater contaminated with persistent insecticides such as diazinon should be treated with suitable physicochemical and/or biological treatment processes such as adsorption [3], chemical coagulation [7], membrane process [8], and bioremediation [9]. However, adsorption and membrane processes just transfer the pollutants from the liquid to solid phase producing secondary waste, which needs further treatment [3,8]. Advanced oxidation processes (AOPs) as talented techniques have more attention to overcome these problems. AOPs commonly include photocatalysis, UV/H_2O_2, UV/O_3, UV/ZnO, UV/TiO_2, and UV/Fenton processes for oxidative destruction and mineralization of organic contaminants [1–4,6,10].

TiO_2 and ZnO nanopowders are widely used as an effective, inexpensive, and nontoxic photocatalysts for the degradation of a wide range of organic chemicals and insecticides [1,2,6,11]. Tungsten trioxide (WO_3) is also a very important semiconductor that provides specific properties [12–14]. And it is applied as solar cells, sensors, electrochromic devices, and photocatalyst [12–14]. Ramos-Delgado et al. [15] reported solar photocatalytic degradation of malathion pesticide with illuminated WO_3/TiO_2 prepared by sol-gel method. They also reported solar photocatalytic degradation of an organophosphorus pesticide by TiO_2 modified with WO_3. Guangjun [16] reported degradation of butyl xanthate with visible light illuminated WO_3. Chu and Rao [17] reported photocatalytic oxidation of monuron herbicides in the suspension of WO_3 under the irradiation of UV-visible light. However, limited information is available for the removal efficiency and removal kinetics of insecticides with illuminated WO_3 nanopowder.

Therefore, in the present work, orthorhombic crystal type of WO_3 was selected as a catalyst in the photocatalytic removal of diazinon. Next, the influence of several operational parameters including WO_3 dosage, pH, diazinon concentration, and organic compounds (humic acid, oxalic acid, phenol, and ethylenediaminetetraacetic acid (EDTA)) concentration on photocatalytic degradation of diazinon were investigated. Finally, kinetic parameters for the photocatalytic degradation were obtained by application of the Langmuir–Hinshelwood (L–H) model. The electrical energy per order (E_{Eo}) was calculated to evaluate cost efficiency of the processes.

2. Materials and methods

2.1. Chemicals

Nanopowder of WO_3 was obtained from Iranian nanomaterial pioneer company in Mashhad city from Iran. It is orthorhombic crystal and has greater than 99.95% purity. The average particle size of the WO_3 particles was 23–65 nm. Humic acid, oxalic acid, phenol, EDTA, and hydrochloric acid, which were of analytical grade, were purchased from Merck. Diazinon, as a model insecticide, was purchased from Chem Service (USA). Its chemical structure and other characteristics are listed in Table 1. The point of zero charge (pH_{pzc}) was determined to investigate the surface charge properties of WO_3. The pH_{pzc} of WO_3 nanocatalyst was determined to adopt the method previously used [18–20].

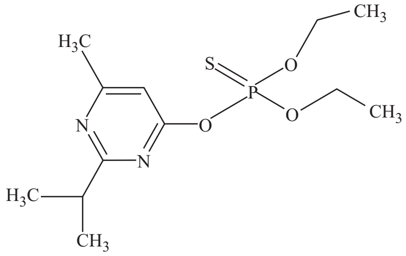
2.2. Experimental setup

The experimental reactor used for the photocatalytic degradation of diazinon is shown in Fig. 1. The reactor was a 2 L photoreactor with working volume of 1 L equipped with a thermocouple to control the temperature of the solution. The solution in the reactor was constantly stirred via a magnetic stirrer. A 125 W medium-pressure UVC lamp emitting maximum wavelength at 247.3 nm was applied as a light source. The light intensity of UVC lamp was equal to 1,020 $\mu w/cm^2$ measured by a Spectroline model DRC-100X digital radiometer combined with a DIX-365 radiation sensor (Shokofan Tosee, Iran).

2.3. Experimental procedure and analysis

In the batch experiments, a selected dosage of WO_3 (0.25–3 g/L) was poured in 1,000 mL of diazinon solution with a certain concentration (5–50 mg/L) at different solution pH ranging from 3 to 11. The initial pH of solution was adjusted by adding NaOH and HCl (0.1 mol/L) and measured by pH meter (Metron, Switzerland). All runs were performed under ambient conditions for 2 h. During the experiments, the solution in the photoreactor was constantly stirred and kept at constant temperature (25 ± 1℃). The solutions loaded with WO_3 suspension were equilibrated in dark condition for 30 min. After the equilibration period, the UV-lamp was switched on and 10 mL of solution was taken at specified time intervals. The aqueous samples were centrifuged (Sigma-301, Germany) at 4,000 revolution per minute (rpm) for 10 min to eliminate WO_3 and then were used to analyze diazinon. The concentration of residual diazinon was determined with a spectrophotometer (UV/Vis Spectrophotometer, Hach-DR 5000, USA) at $\lambda_{max} =$ 295 nm by a calibration curve which was plotted based on Beer-Lambert law [21].

Table 1
Chemical structure and characteristics of diazinon

Structure	
WHO class	II
Density (g/mL at 20°C)	1.11
λ_{max} (nm)	295
M_w (g/mol)	304.3

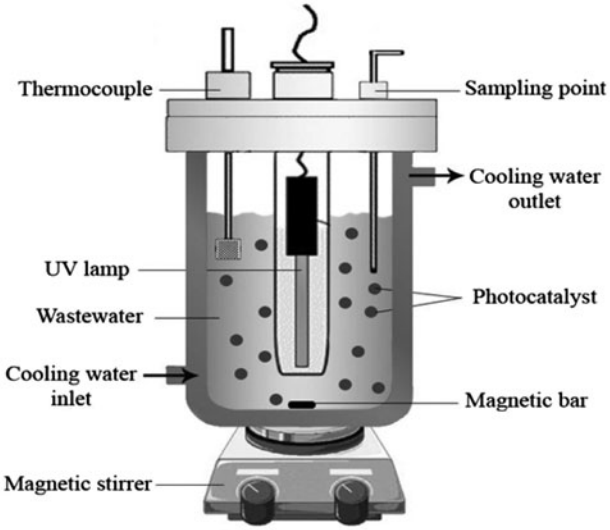


Fig. 1. A schematic flow diagram of the experimental reactor.

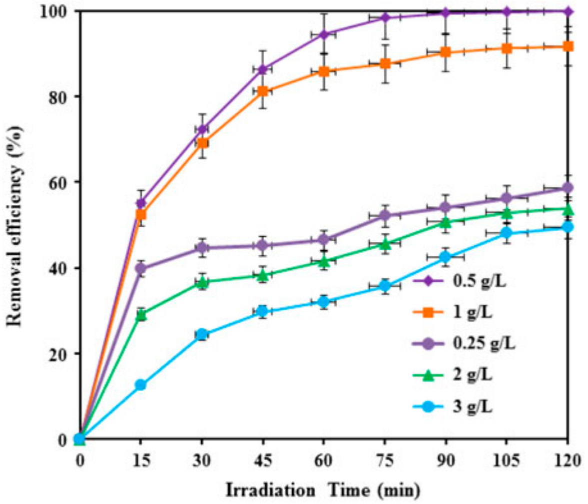


Fig. 2. Effect of nanocatalyst dosage on the photocatalytic degradation of diazinon (pH = 3 and diazinon = 20 mg/L).

3. Results and discussion

3.1. Effect of nanocatalyst dosage

Effect of nanocatalyst dosage on the degradation efficiency was studied at pH equal to 3 and diazinon concentration of 20 mg/L up to 120 min (Fig. 2). Without UV irradiation, the removal efficiency varied from 8.84 to 9.72% depending on the photocatalyst dosage due to an adsorption of diazinon. The most effective degradation of diazinon was observed at 0.5 g/L of nanocatalyst (99.88%), which was chosen as an optimum amount. The total active surface area was enhanced with increasing photocatalyst dosage from 0.25 to 3 g/L. However, turbidity of the suspension was increased, causing more scattering effect and less UV light penetration. Moreover, at high photocatalyst loading, it was difficult to maintain the suspension in homogenous state due to an agglomeration of particles [22–25].

3.2. Effect of pH

Fig. 3 shows that degradation efficiency was decreased by increasing the initial pH from 3 to 11. Indeed, the degradation efficiency was decreased from 99.88 to 19.8% by increasing the initial pH from 3 to 11. At pH values greater than pH_{ZPC} (5.09) of the catalyst, surface becomes negatively charged, thus preventing adsorption of the negatively charged diazinon as well as the hydroxide anion onto the surface; this would be one of the reasons for the reduced degree of

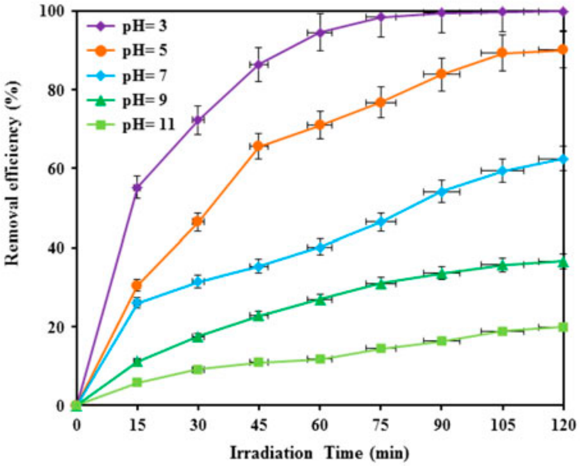


Fig. 3. Effect of initial pH on the photocatalytic degradation of diazinon (dosage = 0.5 g/L and diazinon = 20 mg/L).

degradation at alkaline conditions [26]. Conversely, acidic conditions would favor the degradation of diazinon due to a favorable electrostatic attraction between the positively charged surface and the diazinon [27]. Since the most effective degradation of diazinon was observed at pH 3, further experiments were performed at pH 3. The low photocatalytic efficiency at high pH could be explained by two different factors such as different redox potential and stability of WO_3. Spurgeon et al. [28] reported unstability of WO_3 at high solution pH.

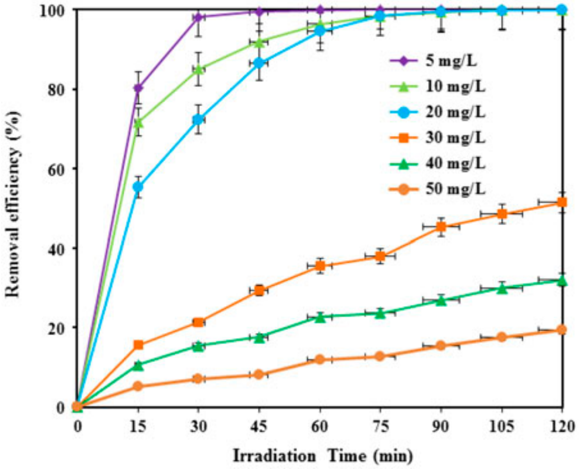


Fig. 4. Effect of initial diazinon concentration on the photocatalytic degradation of diazinon (dosage = 0.5 g/L and pH = 3).

3.3. Effect of initial diazinon concentration

Fig. 4 shows that as the initial diazinon concentration increased, the photocatalytic degradation efficiency decreased. When the initial diazinon concentration increased, more diazinon molecules could be adsorbed on the surface of WO_3. The large amount of adsorbed diazinon and its degradation intermediates might show an inhibitive effect on the further photocatalytic degradation of diazinon because of the presence of decreased free sites on the WO_3 surface for receiving of photons. Moreover, once the concentration of the diazinon increases, it causes more absorption of UV light by diazinon molecules, named as inner filtration effect. This effect causes decrease of photons reaching to the WO_3 surface [17,25]. Similar results have been reported by other researchers [1,29–31]. Overall removal efficiency of diazinon suddenly dropped when the concentration was changed from 20 to 30 mg/L. This result can suggest that photocatalytic efficiency is greatly limited by addition of diazinon above a critical concentration due to combined effects mentioned previously. Considering this experiment, an optimum concentration of diazinon for the near complete removal is regarded as below 30 mg/L.

3.4. Kinetic study and electrical energy determination

The first-order rate constants of photocatalytic process (k_{obs} (1/min)) at different initial concentrations of diazinon are summarized in Table 2. Each experiment was repeated three times and the mean values were reported. The relationship between an initial photocatalytic degradation rate (r) and an initial concentration of organic substrate for a heterogeneous photocatalytic process can be described by Langmuir–Hinshelwood (L–H) model (Eqs. (1) and (2)) [2,24,32,33]:

$$-\frac{\mathrm{d}[\mathrm{Diazinon}]}{\mathrm{d}t} = \frac{k_{\mathrm{c}}K_{\mathrm{Diazinon}}[\mathrm{Diazinon}]}{1+K_{\mathrm{Diazinon}}[\mathrm{Diazinon}]_0} = k_{\mathrm{obs}}[\mathrm{Diazinon}] \tag{1}$$

$$\frac{1}{k_{\mathrm{obs}}} = \frac{1}{k_{\mathrm{c}}K_{\mathrm{Diazinon}}} + \frac{[\mathrm{Diazinon}]_0}{k_{\mathrm{c}}} \tag{2}$$

where $[\mathrm{Diazinon}]_0$ is the initial concentration of the diazinon in mg/L, k_{c} (mg/L/min) is the kinetic rate constant of surface reaction, and K_{Diazinon} (L/mg) is the Langmuir adsorption constant.

The values of K_{Diazinon} and k_{c} were obtained as 0.068 L/mg and 0.006 mg/L/min, respectively. This L–H kinetic model has been used by several authors to analyze heterogeneous photocatalytic reactions.

Table 2
Pseudo-first-order kinetic parameters and E_{Eo} of the photocatalytic degradation of diazinon at different initial diazinon concentrations ($[Diazinon]_0$ = 20 mg/L, catalyst dose = 0.5 g/L, and pH = 3)

$[Diazinon]_0$ (mg/L)	k_{obs} (1/min)	$1/k_{obs}$ (min)	R^2	E_{Eo} (kWh/m^3)
5	0.1233	8.11	0.9951	38.93
10	0.078	12.82	0.9056	61.54
20	0.057	17.54	0.9892	84.21
30	0.005	200	0.9831	960
40	0.002	500	0.9583	2,400
50	0.0001	10,000	0.9834	48,000

For the case of photocatalytic reaction, electrical energy is very important factor for the real application and evaluation for the electrical energy should be provided. Thus, electrical energy was evaluated with electrical E_{EO}. It is defined as the number of kWh of electrical energy required to reduce the concentration of a pollutant by 1 order of magnitude (90%) in 1 m^3 of contaminated water. The E_{EO} (kWh/m^3) can be calculated from the following equation [33,34]:

$$E_{EO} = \frac{p \times t \times 1000}{V \times 60 \times \log\left(\frac{C_i}{C_f}\right)} \tag{3}$$

$$E_{EO} = \frac{38.4 \times P}{V \times k_{obs}} \tag{4}$$

where P is the rated power (kW) of the AOPs system, t is the irradiation time (min), k_{obs} is the pseudo-first-order rate constant (1/min), V is the volume (L) of the wastewater in the reactor, and C_i and C_f is the initial and final diazinon concentrations, respectively. The E_{EO} values for UV-alone, UV/WO_3 processes are reported in Table 3. E_{EO} value for UV/WO_3 process was lower than UV-alone process.

Photocatalytic removal of pesticide in this system was compared with other reports in the viewpoint of electrical energy. For example, Daneshver et al. [2] evaluated the E_{EO} for the photocatalytic degradation of diazinon. In the case of the photocatalytic (particle size 33 and 14 nm) process, the E_{EO} value was 1388.8 and 1,075.3 kWh/m^3 those were less than 20,000 kWh/m^3 calculated by UV process. Wu et al. [35] indicated that the photocatalytic degradation of the pesticide terbufos in TiO_2/UV process could be efficiently achieved with an E_{EO} value of 71 kWh/m^3. Daneshver et al. [36] reported that the photocatalytic degradation of the herbicide erioglaucine in the presence of nanoparticles of TiO_2 irradiated by the UVC light (30 W) could be efficiently achieved with an E_{EO} value of 175.44 kWh/m^3 compared to the 333.333 kWh/m^3 in the photolysis system. This comparison shows that the WO_3/UV process is an effective catalyst for the degradation diazinon from aqueous solution compared to ZnO/UV or TiO_2/UV process.

Table 3
The E_{Eo} values for photodegradation of the diazinon ($[Diazinon]_0$ = 20 mg/L, catalyst dose = 0.5 g/L, and pH = 3)

Process	E_{Eo} (kWh/m^3)
UV	1,038.42
UV/WO_3	91.54

3.5. Effect of the presence of organic compounds

Effect of organic compounds on the removal efficiency of diazinon by WO_3/UV was investigated in the presence of four different organic compounds. Fig. 5 shows that percent removal of diazinon at initial reaction time is oxalate > EDTA > without organic compound > humic acid > phenol. The removed amount of diazinon at initial reaction time in the presence of oxalate and EDTA was greater than that in the absence of any organic additives. One possible reason for the enhanced removal efficiency of diazinon in the presence of oxalate could be explained by the possible photolysis of oxalate that produces various reactive species for the removal of diazinon [37]. However, it was difficult to explain the positive effect of EDTA on the increased degradation efficiency of diazinon. The decreased photocatalytic degradation of diazinon in the presence of humic acid and phenol could be attributed to the interference of the adsorbed organic molecules for the access of diazinon on the surface of photocatalyst. The percent removal of diazinon at

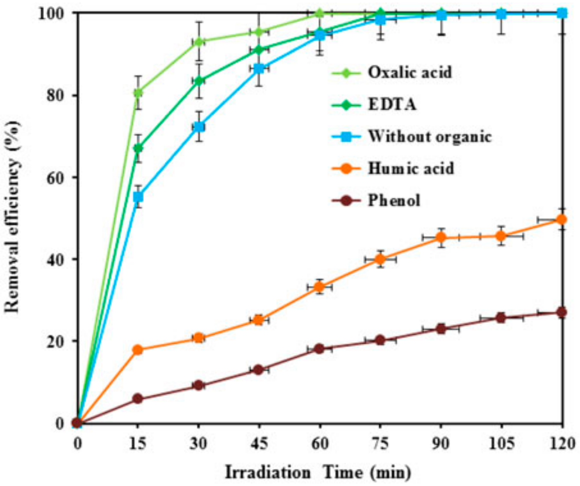


Fig. 5. Effect of the presence of different organic compounds on the photocatalytic degradation of diazinon (dosage = 0.5 g/L, pH = 3, diazinon = 20 mg/L, and organic compounds = 20 mg/L).

initial reaction time ($t = 0$) clearly shows quite decreased adsorption of diazinon on the surface of WO_3 in the presence of humic acid and phenol.

3.6. Comparison of different diazinon removal processes

Diazinon removal by WO_3-alone, UV-alone, and UV/WO_3 processes are shown in Fig. 6. The removal of diazinon through the adsorption process by WO_3-alone was quite low. Overall removal efficiency of diazinon by WO_3-alone and UV-alone processes was 9.57 and 45.56%. But, in the presence of both WO_3 and UV light, 99.88% of diazinon was removed after 120 min. Photolysis was identified as more important removal mechanism of diazinon than adsorption process. However, considering the near complete removal of diazinon in the presence of both UV and WO_3, photocatalytic pathway was also identified as another important removal process. These experiments demonstrate that both UV light and WO_3 are necessary for the effective degradation of diazinon.

Based on the above experiments and analysis, the mechanism of the photocatalysis could be proposed as following:

When WO_3 is illuminated with the UV light ($\lambda < 390$ nm), an electron excites from the valence band to the conduction band to give separation of electron and hole [12,38–40] (Eq. (5)):

$$WO_3 + h\upsilon \rightarrow WO_3\left(e^-_{CB} + h^+_{VB}\right) \quad (5)$$

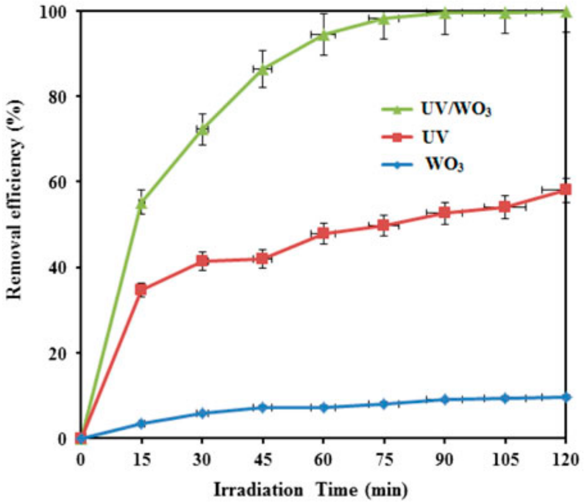


Fig. 6. The contribution of each process involved in the photocatalytic degradation of diazinon (dosage = 0.5 g/L, pH = 3, and diazinon = 20 mg/L).

And positive hole reacts with H_2O or OH^- to generate highly reactive radical species like hydroxyl radicals, which can oxidize organic contaminants and their degradation intermediates. Besides, holes can oxidize various pollutants directly, too.

$$h^+_{VB} + \text{insecticide} \rightarrow \text{insecticide}^{\cdot+} \rightarrow \text{oxidation of the insecticide} \quad (6)$$

$$h^+_{VB} + H_2O \rightarrow H^+ + {}^{\cdot}OH \quad (7)$$

$$h^+_{VB} + OH^- \rightarrow {}^{\cdot}OH \quad (8)$$

$$h^+_{VB} + H_2O \rightarrow H^+ + {}^{\cdot}OH \quad (9)$$

$^{\cdot}OH$ + insecticide to degradation of the insecticide

The temporal distribution of species from the decomposition of diazinon in aqueous solution by advance oxidation process such as ozonation and UV/H_2O_2 at different pH was reported by other researchers [41,42]. They reported formation of sulfate, phosphate, carbonate, and nitrate ions. The sulfur groups might be easily detached from the diazinon molecules and could be oxidized to sulfate ions. From the decomposition of organophosphorus pesticides by advance oxidation process, similar results have been reported [2,6,43,44].

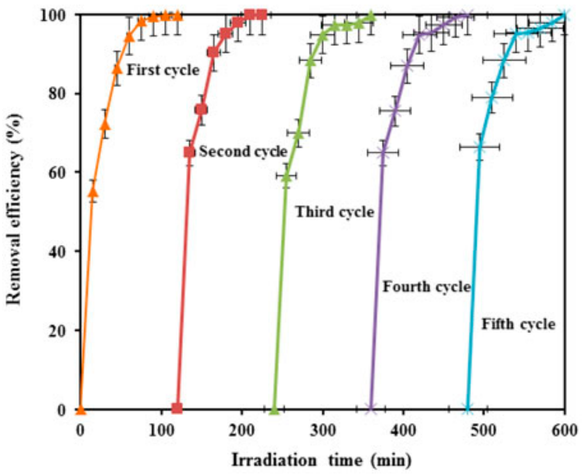


Fig. 7. The results of reusability test for the photocatalytic degradation of diazinon within five repeated cycles (dosage = 0.5 g/L, pH = 3, and diazinon = 20 mg/L).

3.7. *Reusability of nanocatalyst*

The ability of a photocatalyst for continuous removal of organic contaminants is a significant criterion. Hence, the photocatalytic degradation of diazinon was performed by UV/WO_3 for five repeated runs. As can be seen in Fig. 7, the regenerated photocatalyst showed the same photocatalytic activity up to fifth run.

4. Conclusions

In this study, application of WO_3 was considered for the photocatalytic degradation of diazinon in aqueous solutions. As the catalyst dosage was increased to 0.5 g/L, the removal of diazinon was continuously enhanced, but decreased at dosages above 0.5 g/L. Removal efficiency decreased by increasing pH and initial diazinon concentration. Electrical E_{EO} was increased and reaction rate constant was decreased with increasing initial diazinon concentration. The presence of organic compounds such as humic acid and phenol hindered the photocatalytic degradation of diazinon. However, it was increased in the presence of oxalic acid and EDTA which may produce additional oxidant during photocatalytic degradation of diazinon. The electrical energy consumption per order of magnitude for photocatalytic degradation of diazinon was lower in the UV/WO_3 process than UV-alone and WO_3-alone process, which confirmed the better performance of UV/WO_3 process.

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