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Degradation and mineralization of diazinon pesticide in UVC and UVC/TiO_2 process

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ABSTRACT

The performance of photolytic and photocatalytic degradation and mineralization of diazinon in water using UVC and UVC/TiO_2 process in batch condition was investigated, determining the effects of different parameters. The best pH in removal of diazinon by UVC-Photolysis and UVC/TiO_2 process is equal to 5 and optimum amount of catalyst was calculated as 150 mg/L. The results showed that diazionon completely degraded after 30 min at 100 mg/L TiO_2 and pH 5. The presence of anionic species promoted the photolysis efficiency to degrade diazinon from 52 to 80%, lowering the UVC/TiO_2 ability to degrade and mineralize diazinon from 97 to 62%, on the other hand. Mineralization of diazinon by photocatalyst process proved to be 2.5 times higher than of photolysis. Moreover, the reduction pattern in the photocatalysis and photolysis processes were better described by pseudo-first- and second-order kinetics model with a reaction rate constant of 0.094 and 0.0029, respectively.

Keywords: UV irradiation; Photocatalysis; TiO_2 nanoparticle; Diazinon

1. Introduction

In recent years, major concerns about the presence of insecticides in the environment have been expressed. These compounds as a toxic one, has carcinogenic effect, toxicity on the central nervous system, and the reproduction system [1]. Diazinon is classified by the World Health Organization as "moderately hazardous" class II. It was related with toxicity to aquatic organisms at concentration of 350 ng/L [2]. Water contaminated with diazinon being carried by floodwater and their fate in the environment depends on different factors including volatilization, hydrolysis, and photolysis [3]. Diazinon is relatively water-soluble, non-polar, moderately stimulant, and resistant in soil [4]. Thus, the presence of diazinon in surface and ground water is concerning [4]. Unfortunately, conventional systems are not able to remove this insecticide [5].

UV irradiation is one of the most well-known disinfection processes, having extensive uses due to simplicity and effectiveness [6]. In addition to disinfection ability of UV_{254}, it acts as a radical inducer in surface water containing soluble ions. In previous studies, the photolysis degradation of diazinon was surveyed with different results reported. Kouloumbos et al. surveyed photolysis of diazinon with a medium pressure lamp emitting wavelength mainly at 300–400 nm, which is

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far from the diazinon adsorption light edge [7]. Derbalah and Ismail showed that a 80 W medium pressure lamp only removed 40 percent of diazinon after 200 min irradiation [8]. According to the previous results, several factors justified the insufficiency of photolysis in degradation of diazinon including inappropriate wavelength. The results generally show UV as partially able to degrade diazinon while requiring more time or auxiliary processes (combine with catalyst) in order to complete the degradation process. To conquer these problems, advanced oxidation processes (AOP) have been used as complementary techniques. Overall AOPs, generating hydroxyl radical ($^{\cdot}OH$) have been widely used to destroy insecticides that cannot be removed by conventional methods [9]. The hydroxyl radical can be generated in aqueous solutions using O_3/UV, H_2O_2/UV, UV/TiO_2 etc. [9,10]. Among these methods, photocatalytic reaction using UVC/TiO_2 is more efficient. Chlorpyrifos, cypermethrin, and chlorothalonil [11–13], metaldehyde [14], pyridaben [15], Fenhexamid [16] are among the recalcitrants being removed by UVC/TiO_2 process. Ruey-an Doong et al. showed UV-TiO_2 inefficacy to degrade diazinon as related to UV-TiO_2/H_2O_2 [17]. Previous studies suggested that UV-TiO_2 has better degradation efficiency as related to UV irradiations, yet surface water contains more anion species that can have a suppressive or rising effect on the process efficiency which might change the reported trend.

Therefore, the aim of the study is to investigate the performance of photocatalytic degradation of diazinon in water using UVC and UVC/TiO_2 processes. In this regard, the effect of pH, diazinon concentration, catalyst loading, and the presence of anions, as well as radical scavengers on mineralization efficiency and kinetic of reactions in the process of UVC and UVC/TiO_2 were determined.

2. Materials and methods

2.1. Catalyst characterization

TiO_2 (a 90/10 mixture of rutile and anatase) was obtained from Degussa corporation. The specific surface area of the TiO_2 particles was greater than 106 m^2/g. The average size of crystallite was calculated based on Debye–Sherrer's formula:

$$D = \frac{k\lambda}{\beta \cos\theta} \tag{1}$$

where β is the full width at half maximum peak intensity, k is a coefficient equal to 0.9, θ is the diffraction angle in radians, and λ is the X-ray wavelength of Cokα radiation. Based on the Sheerer formula, size of TiO_2 nano-crystallites were found to be equal to 26.3 nm.

Fig. 1 shows the surface and shape of the catalysts using Ziess (Germany) scanning electron microscopy (SEM). As shown in Fig. 1, the purchased TiO_2 has approximately spherical shape with purity up to 99%.

2.2. Photolytic and photocatalytic experiments

Fig. 2 shows the experimental procedures. Diazinon standard stock solution (25 ppm) was prepared in deionized water and stored at dark and 4℃. The experimental setup for photocatalytic reactor used in this study is shown in Fig. 3. A 9 W low-pressure mercury UV-lamp (Philips, Holland) emitting maximum wavelength at 254 nm and light intensity equal to 2.2 mW/cm^2 was used as the radiation source. The UV lamp was surrounded with a quartz sleeve. The distance between UV source and solution was 2 cm in all experiments. In order to determine photolysis efficiency in degrading diazinon, 100 mL of predetermined concentration of diazinon solution was irradiated and after measuring diazinon concentration at the end of radiation, the removal efficiency was obtained.

Due to hydrolysis effect of pH, the photolysis experiments were carried out at the pH range of 2–11. The desired pHs were adjusted by adding proper amount of 0.1 M HCl and NaOH solutions. All photocatalytic experiments were performed with 100 mL solution. The reaction oxygen was provided through shaking with a magnet stirrer, being stirred at 100 rpm. The dark experiments were performed under the above-mentioned conditions while turning the lamp off.

In order to determine photocatalytic experiments, 100 mL of predetermined concentration of diazinon solution was mixed with proper aliquots of sonicated TiO_2 suspension solution. During experiments, the solution in the reactor was constantly stirred. The effect of pH was examined with variation of the solution pH (5, 7, and 9), initial diazinon concentration of 10 mg/L and catalyst loading of 100 mg/L. As a result of catalyst amount effect, experiments were done at 10 mg/L diazinon concentration, pH 7, and different catalyst loading (10, 25, 50, 100, 150, and 200 mg/L). Also, degradation of different concentrations of diazinon were done at pH 7, 100 mg/L TiO_2, and 5, 10, 20 mg/L diazinon solution. Effect of the presence of anions $(SO_4^{-2}, CO_3^{-2}, PO_4^{-3}, \text{and } Cl^{-1})$ with concentration of 3 mM and 0.5 g tert butyl on the diazinon

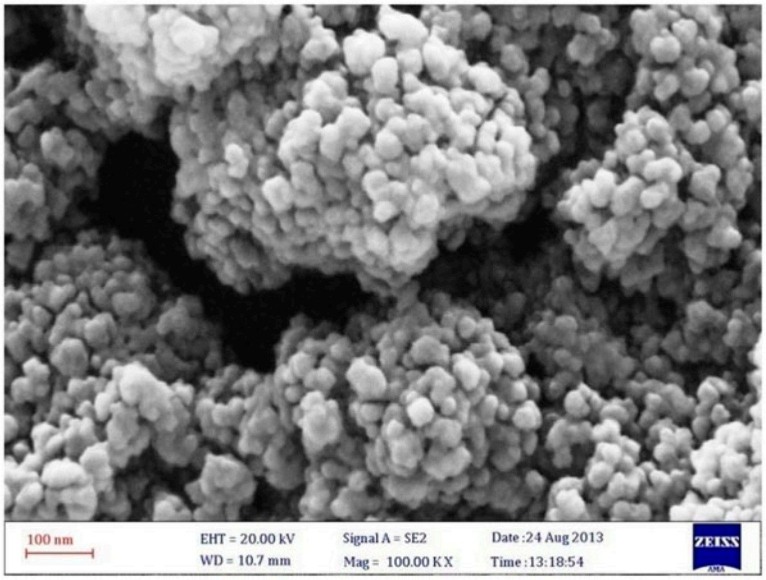

Fig. 1. SEM micrograph of purchased TiO_2.

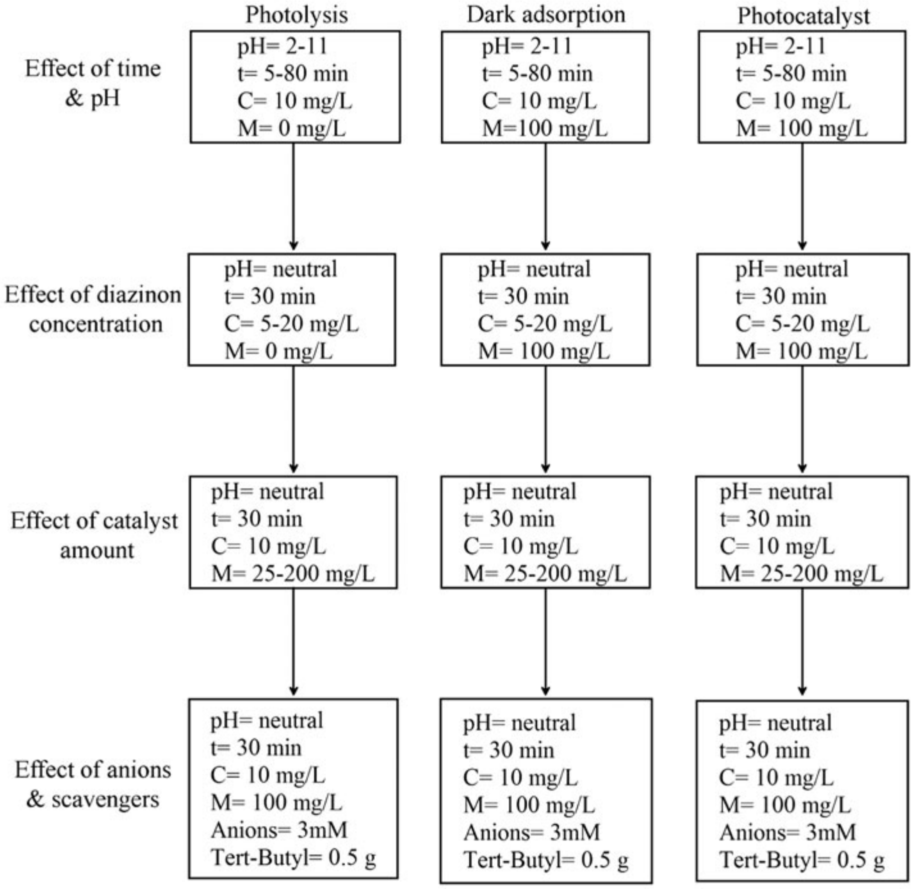

Fig. 2. Schematic diagram of experimental procedures.

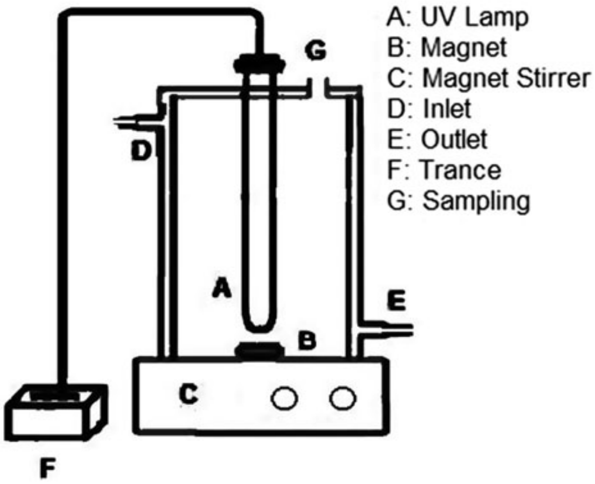

Fig. 3. Schematic diagram of the reactor.

degradation at the pH 7, 10 mg/L diazinon solution, and 100 mg/L TiO_2 was studied as well.

2.3. Chemicals and analysis

Diazinon (99% purity), was provided by Sigma-Aldrich Chemie GmbH (Germany). All other chemicals were of analytical grade. A 3501 pHmeter (Jenway Instrument, United Kingdom) was used to measure the solution pH. At the end of reactions, the withdrawn sample suspension were first centrifuged at 15,000 rpm (Universal 320, Hettich Germany) for 15 min, then filtered through 0.2 µm acetate cellulose filter to remove TiO_2 nanoparticles and then residual diazinon concentration was analyzed. Diazinon concentration was analyzed by spectrophotometer (UV/Vis Spectrophotometer, Perkin-Elmer 550 SE, USA) at $\lambda_{\max}$ of 248. The removal efficiency was calculated as follows:

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

where C_0 and C_e are diazinon concentrations at the initiation and the end of reaction, respectively.

The degree of diazinon mineralization in photolysis and photocatalysis was measured by determining the total organic carbon (TOC) of the solution using a TOC analyzer (Shimadzu) before and after the processes. The mineralization efficiency of diazinon was calculated as follows:

$$\text{Mineralization Efficiency } (\%) = \frac{\text{TOC}_0 - \text{TOC}_t}{\text{TOC}_0} \times 100 \quad (3)$$

where TOC_0 and TOC_t denote the TOC concentrations before and after oxidation, respectively.

3. Results

3.1. Removal of diazinon at different solution pH

The influence of solution pH on the photocatalytic degradation is an important aspect of the study. The effect of this parameter on the efficiency of photocatalytic and photolysis process was studied by varying the solution pH. Fig. 4 shows the removal efficiency of diazinon in UVC process at a pH solution ranging from 2 to 11 and fixed reaction time (30 min). The maximum diazinon removal efficiency in photolytic and photocatalytic processes was acquired at pH 5.

As efficiency of photocatalytic process is time dependent, in this study, effect of reaction time was determined at 5 min interval time lapses and pHs of 5, 7, and 9. The results illustrated in Fig. 5 show that there is a gradual increase as the reaction time increases andafter 30 min in pH equal to 5, 7, and 9, removal efficiency acquired was 100, 97, and 87%, respectively.

There is a gradual increase in removal efficiency with increasing pH up to 5 and then it began to fall off. Based on moussavi et al. [18] previous study, it is obvious that the direct hydrolysis of diazinon at different pHs (without radiation source) have a significant impact on the reported trend. Furthermore, in acidic pH, adding hydrogen to the sulfur atom would result in the protonation of diazinon [2].

Generally, there are several factors to explain the effect of pH on the photocatalytic process. It was reported that the recombination of electron-hole pairs at the surface of TiO_2 can complete within 10^{-9} s,

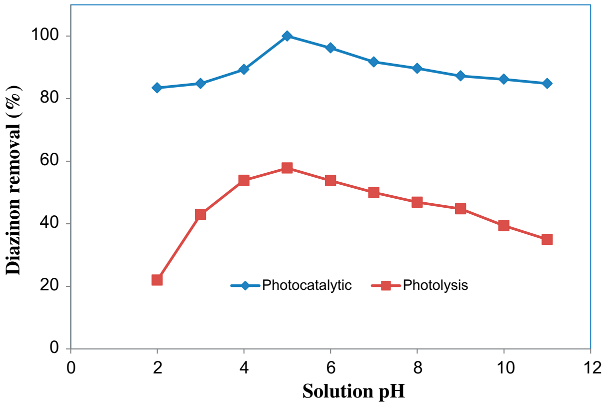

Fig. 4. Effect of pH on photocatalytic and photolysis degradation of diazinon at fixed reaction time 30 min (TiO_2 = 100 mg/L; diazinon = 20 mg/L).

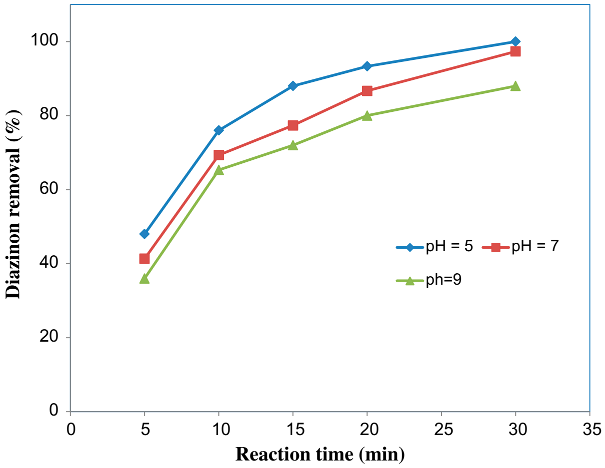

Fig. 5. Effect of pH on photocatalytic degradation of diazinon (TiO_2 = 100 mg/L; diazinon = 10 mg/L).

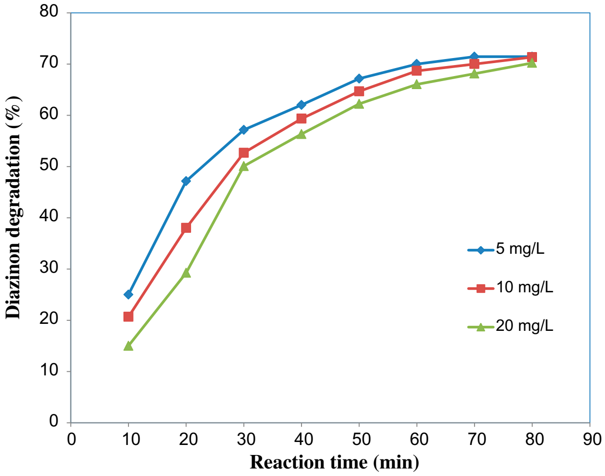

Fig. 6. Effect of initial diazinon concentration on the removal of diazinon by UVC (pH = natural).

which implicit that the contaminants could not be degraded unless they are adsorbed on the surface of nanoparticle [19]. Thus, surface adsorption process in controlling the degradation of diazinon is of significant importance [19]. The main effective factor in adsorption of diazinon on the TiO_2 surface is electrostatic mechanism. It has been reported that the pH of zero point charge (pH_{ZPC}) for TiO_2 is 6.5 [20]. According to the Eqs. (4) and (5), in the lower and higher pH than $pH_{ZPC,}$ TiO_2 surface will be positive and negative charge, respectively [21]

$$pH < pH_{zpc} : TiOH + H^+ \rightarrow TiOH_2^+ \qquad (4)$$

$$pH > pH_{zpc} : TiOH + OH^- \rightarrow TiO^- + H_2O \qquad (5)$$

The given pK_a for diazinon is 2.6 [22]. Diazinon is negatively charged above pH 2.6, whereas catalysts are positively charged below pH 6.5. As expected, maximum removal conditions will be at $pK_a^{diazinon} < pH < pH_{ZPC}^{TiO_2}$. Since natural pH of contaminated water with diazinon is around 7, the further experiments were performed with pH 7.

3.2. *Removal of diazinon at different concentration of diazinon*

The removal efficiency of diazinon in photolysis (Fig. 6) and photocatalysis (Fig. 7) processes was investigated with variation of initial diazinon concentration (5, 10, and 20 mg/L) at constant TiO_2 dosage of 100 mg/L and initial pH of 7. The diazinon removal efficiency in photolysis did not exceed 70 percent (after 80 min), however taking benefit of TiO_2 as the catalyst, the complete removal were acquired only after 40 min. In photolysis process, because of narrow thickness of solution (between quartz sleeve and the glass wall) and also well mixing, only little difference in diazinon removal efficiency was observed at different solution initial concentrations.

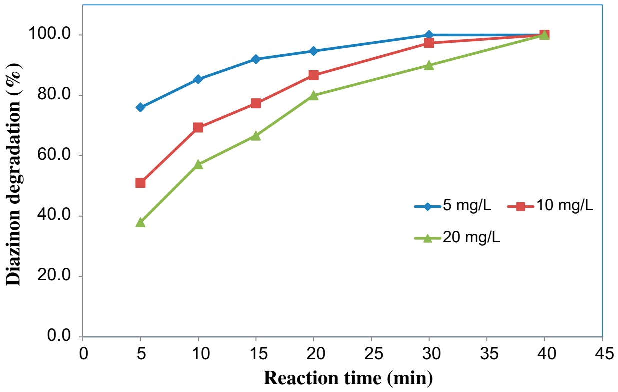

Fig. 7. Effect of initial diazinon concentration on the removal of diazinon by UVC/TiO_2 (pH = natural; catalyst dosage = 100 mg/L).

Survey of different solution concentrations in photocatalysis showed a significant difference between the removal efficiency, especially at initial reaction time. When initial concentration of solution increases, greater amounts of diazinon are adsorbed on the surface of TiO_2, so formation of hydroxyl radicals will be reduced because there are fewer active sites for adsorption of hydroxyl ions [22]. Furthermore, since the amount of catalyst is constant, the increase in surface coverage due to solution concentration will make fewer numbers of diazinon molecules affected by $^{\cdot}OH$ [23,24]. It should be mentioned that since the photons are snatched before they can reach the catalyst surface so as the concentration of diazinon increases, the removal efficiency begins to drop [22].

3.3. Removal of diazinon at different catalyst loading

In Fig. 8 efficiency of UVC/TiO_2, adsorption by TiO_2 and synergistic effect of UVC/TiO_2 at different catalyst loading has been shown. Experiments performed with different concentrations of TiO_2 showed removal efficiency increasing with an increase in TiO_2 concentration up to 150 mg/L, but further increase in the amount of TiO_2 caused the photocatalytic process efficiency decreases due to light obstruction by the TiO_2. Difference sum of the adsorption and UVC of UVC/TiO_2 indicates synergistic effect of UVC/TiO_2. Removal efficiency of diazinon at constant time (30 min) in UVC is 52.7%, whereas in adsorption and UVC/TiO_2, in 100 mg/L TiO_2, are 28.7 and 97.3%, respectively. Thus, synergistic effect of UVC/TiO_2 is 15.7%.

In line with increasing catalyst loading, the total active surface area increases. On the other hand, due to increase in the turbidity of the suspension, UV light penetration was decreased. Furthermore, agglomeration occurred at high catalyst loading TiO_2, causing difficulty in retaining the suspension homogenous and lowering the number of active sites [23,25].

3.4. Effect of the presence of radical scavengers

In Figs. 9 and 10 efficiency of UVC/TiO_2 and photolysis in the presence of different radical scavengers has been shown, respectively. Experiments performed in the presence of different radical scavengers showed a decrease in the removal efficiency of diazinon in UVC/TiO_2. As shown in Fig. 9, removal efficiency of diazinon by UVC/TiO_2 in the absence of radical scavengers was 97.3%, while in the presence of tert butyl, removal efficiency reached 62%. The inhibition efficiency of the studied scavengers was as follows: carbonate < phosphate < sulfate < chloride < tert butyl.

As shown in Fig. 10, diazinon removal efficiency of photolysis in the absence of radical scavengers was 52.3% while adding anionic scavengers enhanced the removal efficiency to 67.5%. UVC light made possible the conversion of radical scavengers into anion radicals that their oxidation power is more than that of sole UVC irradiation [23,24].

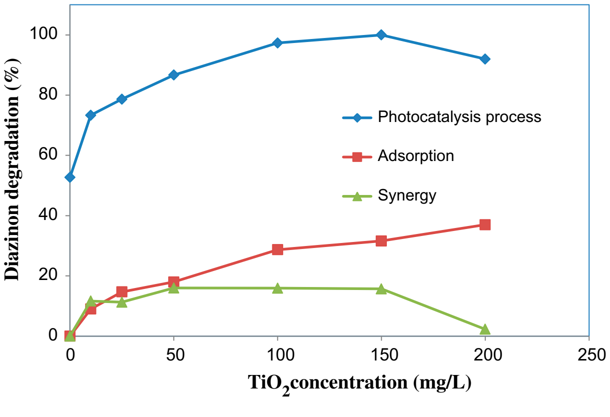

Fig. 8. Efficiency of UVC/TiO_2, adsorbtion by TiO_2, and synergistic effect of UVC/TiO_2 at different catalyst loading (time = 30 min; pH = natural; diazinon = 10 mg/L).

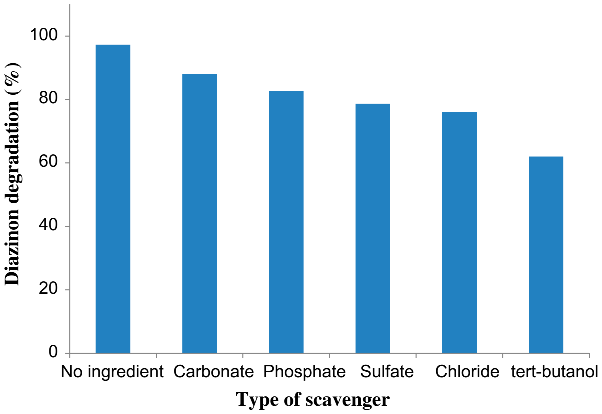

Fig. 9. Effect of the presence of radical scavengers on the photocatalytic degradation (time = 30 min, pH = natural; diazinon = 10 mg/L; TiO_2 = 100 mg/L).

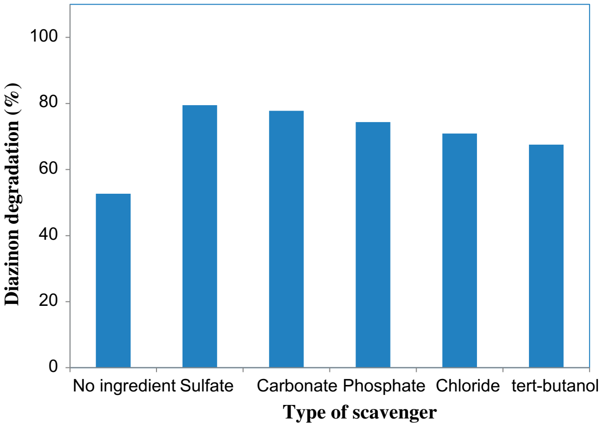

Fig. 10. Effect of the presence of radical scavengers on the photolysis degradation (time = 30 min; pH = natural; diazinon = 10 mg/L).

According to the results, adding different radical scavengers to the photocatalytic process suppressed the removal efficiency. In fact, radical scavengers react with hydroxyl radical transforming to anion radicals (Eqs. (6)–(8)), while oxidation power of anion radicals is much less than hydroxyl radicals [26].

$$SO_4^{2-} + {}^{\cdot}OH \rightarrow SO_4^{\cdot-} + OH^- \tag{6}$$

$$HCO_3^{2-} + {}^{\cdot}OH \rightarrow CO_3^{\cdot-} + H_2O \tag{7}$$

$$CO_3^{2-} + {}^{\cdot}OH \rightarrow CO_3^{\cdot-} + OH^- \tag{8}$$

On the other hand, adding anionic scavengers enhanced the removal efficiency. UVC light causes conversion of radical scavengers into anion radicals that their oxidation power is more than of sole UVC irradiation [26].

In addition, photolysis process mechanism in reaction with organophosphorus pesticides is desulfuration of double bond P=S and oxidizing to P=O bound. The final product of this reaction is benzoic acid or Sulfuric acid [27]. In fact, these radicals cause oxidation of sulfur atom with separate one electron [27]. Moreover, these compounds can increase the sensitivity of diazinon against UVC, which is defined as photosensitized degradation [26].

3.5. Mineralization of diazinon by UVC/TiO_2 and UVC

The mineralization of diazinon was determined by measuring the TOC with a Shimadzu Model TOC-5050A. Fig. 11 shows the mineralization of diazinon in UVC/TiO_2 and UV photolysis processes. According to Fig. 11, mineralization of diazinon by UVC/TiO_2 and photolysis after 30 min was reported 44.2 and 17.6%, respectively, implying that the mineralization by UVC/TiO_2 is much more than by photolysis.

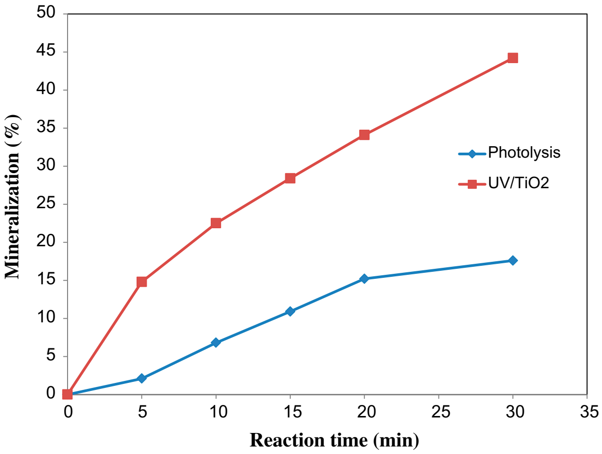

Fig. 11. Mineralization of diazinon by UVC/TiO_2 and UVC (photolysis) process.

As observed, photocatalysis process showed more mineralization efficiency over photolysis process; the unselective attaches of ${}^{\cdot}OH$ radicals and its high oxidation potential of 2.80 V accounts for the higher mineralization power of photocatalysis process.

3.6. Kinetics of photocatalytic and photolysis degradation of diazinon

Most commonly used kinetic expression to explain the kinetics of the heterogeneous catalytic processes is Langmuir–Hinshelwood (LH). This model establishes the relationship between reaction rate and concentration of a reactant [28,29]. The surface coverage (θ) was related to the initial concentration of the substrate (C) and adsorption equilibrium constant (K) through the following equation:

$$\theta = \frac{KC}{1 + KC} \tag{9}$$

The reaction rate can be expressed as follows:

$$Rate = \frac{dC}{dt} = K_{LH}\theta = \frac{K_{LH}KC}{1 + KC} \tag{10}$$

where, K_{LH} is the photocatalytic reaction rate constant. The photocatalytic degradation of diazinon with UVC/TiO_2 follows the pseudo-first-order kinetics at low initial diazinon concentration [30]. The calculated values of k_{app} and the linear correlation coefficient (R^2) for photocatalytic process are presented in Table 1. Accordingly, the values of K_{app} verify the higher efficiency of the TiO_2 nanoparticle related to the others, especially ZnO to remove diazinon from aqueous solution. Daneshvar et al. [22] used a 30 W UV-C lamp

Table 1
Pseudo-first-order kinetic parameters for the photocatalytic removal of diazinon by TiO_2 nanoparticle at different initial diazinon concentration (TiO_2 = 100 mg/L; pH = natural)

Diazinon concentration (mg/L)	k_{app}	R^2
5	0.102	0.994
10	0.094	0.991
20	0.073	0.993

Table 2
Kinetic parameters for the photolysis removal of diazinon at different initial diazinon concentration (pH = natural)

	5 mg/L		10 mg/L		20 mg/L	
Reaction order	R^2	k	R^2	k	R^2	k
Zero-order	0.828	0.036	0.884	0.079	0.891	0.17
First-order	0.94	0.015	0.944	0.014	0.915	0.013
Second-order	0.97	0.0057	0.982	0.0029	0.978	0.0014

and ZnO nanoparticle to remove diazinon from aqueous solution with the obtained reaction rate constant at 20 ppm diazinon concentration being 0.021 which is lower than UVC/TiO_2 rate constant of the present study.

In order to obtain the kinetic model in photolysis process, the experimental data were fitted with zero, first, and second-order equations. From this evaluation, the oxidation pattern of diazinon was better described by second-order kinetic model. The calculated values of reaction rate constant (k) and the linear correlation coefficients (R^2) for photolysis process are presented in Table 2.

4. Conclusion

The efficiency of UV-C photolysis and UV-TiO_2 photocatalyst to diazinon removal from aqueous solution were investigated, with the effect of different conditional parameters being determined. Optimum catalyst loading rate was equal to 150 mg/L which was led to 15.7% synergistic effect over photolysis process. The presence of radicals in UV-TiO_2 process was verified by using different radical scavengers. Mineralization of diazinon by UVC/TiO_2 and photolysis after 30 min were equal to 44.2 and 17.6%, respectively. The results of this study showed that the photocatalytic process using UVC/TiO_2 can be used as an efficient and promising way to remove pesticides from contaminated waters.

Acknowledgment

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