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Degradation of the fungicide carbendazim in aqueous solutions with UV/TiO_2 process: Optimization, kinetics and toxicity studies

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Abstract

An attempt was made to investigate the potential of UV-photocatalytic process in the presence of TiO_2 particles for the degradation of carbendazim ($C_9H_9N_3O_2$), a fungicide with a high worldwide consumption but considered as a "priority hazard substance" by the Water Framework Directive of the European Commission (WFDEC). A circulating upflow photo-reactor was employed and the influence of catalyst concentration, pH and temperature were investigated. The results showed that degradation of this fungicide can be conducted in the both processes of only UV-irradiation and UV/TiO_2; however, the later provides much better results. Accordingly, a degradation of more than 90% of fungicide was achieved by applying the optimal operational conditions of 70 mg L^{-1} of catalyst, natural pH of 6.73 and ambient temperature of 25 °C after 75 min irradiation. Under these mild conditions, the initial rate of degradation can be described well by the Langmuir–Hinshelwood kinetic model. Toxicological assessments on the obtained samples were also performed by measurement of the mycelium growth inhibition of *Fusarium oxysporum* fungus on PDA medium. The results indicate that the kinetics of degradation and toxicity are in reasonably good agreement mainly after 45 min of irradiation; confirming the effectiveness of photocatalytic process.

Keywords: Photocatalytic degradation; Carbendazim; TiO_2; Kinetics; Toxicity; Pesticide

1. Introduction

The processes and technologies available at the present time for the treatment of polluted water are varied. The wastewater treatment techniques, most frequently used, can be divided into physical, biological and chemical. Usually, wastewaters are only treated with physical and biological techniques which greatly reduce the pollution, but not enough to comply with current standards which are becoming stricter more and more. The tendency is toward greater use of chemical treatment, both to comply with standards and to recycle used water which is the great goal for the future. In this regard, wastewaters containing pesticides cannot very often be treated by biological techniques, since they are toxic for the microorganisms and therefore their biodegradation is impossible [1].

Advanced oxidation processes (AOPs) are chemical oxidative processes which can be applied to wastewater treatment to oxidize pollutants. The hydroxyl radical, generated in these processes, is the second strongest known oxidant ($E^{\circ} = 2.72$ V and 1.89 V vs. standard hydrogen electrode at pH 0 and 14, respectively) after fluorine. It is able to oxidize and mineralize most organic molecules with high second-order rate constants of 10^6–10^9 M^{-1} s^{-1} depending on the chemical structure of the substrate [2]. The reactions by which hydroxyl radicals attack organic molecules are hydrogen abstraction, electrophilic addition, electron transfer and also radical–radical reactions [3].

A lot of studies have been conducted to investigate the use of advanced oxidation processes using semiconductor metal oxides as photocatalysts, especially in water detoxification [4,5]. Up to now, TiO_2 has been the dominant semiconductor photocatalyst, although many other types of semiconductor photocatalysts are available [6]. The domination of TiO_2 in this field can be attributed to its superior photocatalytic oxidation ability and non-photo-corrosive, nontoxic and inexpensive characteristics. Very small concentration levels of pollutants at ambient temperatures and atmospheric pressure are usually degradable, using photocatalytic methods with irradiation in UV region [7].

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Carbendazim is a systemic benzimidazole fungicide with an extensive and widespread use. Under natural environmental conditions, it is very stable [8] and it has been frequently detected in surface waters [9]. Meanwhile, it appears as the active substance of benomyl and thiophanate-methyl fungicides and moreover as the main degradation product of these two compounds [10]. This substance is classified by the World Health Organization (WHO) as "unlikely to present hazard in normal use" [11]. This product is toxic for humans, animals and plants [8]. The exposure to this substance is considered to be within acceptable levels [12]. Pesticide-containing wastes are formed at almost every stage of pesticide production or use [13]. carbendazim may similarly be found as a pollutant of water resources where it can accumulate, it is of great interest to investigate to process leading to its elimination.

The photo-degradation of carbendazim has been studied under different experimental conditions of irradiating with UV light, both in the absence and in the presence of hydrogen carbonate ions [2,8,14]. The existence of different reaction sites for carbendazim induced degradation has also been studied [2]. Recently, the use of synthetic and natural dye pigments, as "photosensitizers" has been investigated for the visible-light photo-degradation of the colorless solution of this fungicide and also several 2-substituted benzimidazoles [9]. The overall result of photo-degradation of fungicide and photo-protection of the sensitizer is reported.

In this study the photocatalytic degradation of carbendazim and the influence of various operating parameters on decomposition rate are examined. This fungicide is to be depredated in the presence of commercial ordinary TiO_2 particles and irradiated by the UV light in a suspended and circulated reactor. The usefulness of degradation progress is to be assessed by the toxicological investigations.

2. Experimental

2.1. Reagents

All reagents were used as received without further purification. The carbendazim fungicide $C_9H_9N_3O_2$ (methyl-2-benzimidazole carbamate, CAS No.: 10605-21-7, MW = 191.19) was provided from Suzhou World-best Agro-Biochemical company with purity of more than 98% (white powder). The molecular structure of this fungicide is shown in Fig. 1. TiO_2 catalyst was Merck product in the anatase form (99%); with the BET surface area of 14.68 $m^2\,g^{-1}$ and the average particle diameter of 27.6 μm [15]. Acidic or alkaline media were obtained by addition of solutions of either HCl or NaOH (Merck products) to the aqueous solutions containing the substrate. Distilled water was used to prepare the solutions.

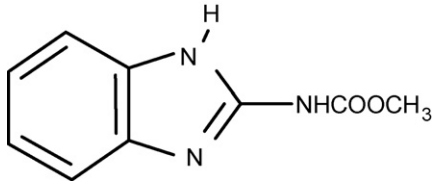

Fig. 1. Chemical structure of carbendazim.

2.2. Photocatalytic reactor

A circulating upflow annular and symmetric vertical photoreactor with a conic body shape without dead-zone and a capacity of about one liter was used. The details are given in our previous works [16,17]. The UV lamp was positioned centrally in the reactor, surrounded directly by the solution and therefore the maximum light utilization was achieved. The UV lamp (16.5 cm body length and 8 cm arc length) was mercury 250 W in the wavelength range of 280–400 nm and the maximum lamp emission of 365 nm (measured by a TOPCON UV-R-1 spectroradiometer). The reactor was equipped with a water-flow jacket for regulating the temperature, by means of an external circulating flow of a thermostat bath, having an accuracy of ±0.1 °C. A pump, located below the reactor, provides an adjustable circulating upflow stream, receiving the solution from top of the reactor and delivering to bottom, below the lamp. In this way, both the well-mixing (the circulating pump delivers a flow-rate of about 5200 mL min^{-1}) and fluidizing of catalyst particles were provided around the quartz tube. The whole reactor body was covered with reflectors of polished aluminum thin layer. Since the photocatalysis is sustained by a ready supply of dissolved oxygen, air was supplied to the reaction system at a constant flow-rate using a micro-air compressor.

2.3. Photocatalytic experimental procedure

In order to perform the experiments, a solution containing 10 mg L^{-1} of carbendazim (about 5×10^{-5} M), initially prepared by warming the solution, and a known amount of TiO_2 concentration was prepared. The pH was adjusted to the desired value by means of a pH meter (Denver, uv-10) using dilute HCl and NaOH solutions. To initiate the degradation, the solution was transferred to the reactor and the lamp was switched on while adjusting the temperature. During each experiment, circulation of suspension was maintained to keep suspension homogenous and to have uniform temperature. Samples (4 mL) were taken at regular time intervals and then centrifuged, in order to separate the TiO_2 particles from the samples.

Analysis were performed, after separation of the photocatalyst particles by centrifugation, with a UV–vis spectrophotometer (PerkinElmer, 55 OSE), measuring the absorbance at appropriate maximum wavelength (λ_{max}) which varies from 277 nm to 285 nm at different pH values of 3–9, respectively, and using the appropriate calibration curves (Fig. 2). The reason for the shift of maximum wavelength with pH can be due to the electron transfers in amine groups attached to the benzene ring at different pH values [18]. A considerably increase in absorbance is observed as the pH increases. The operative conditions of experiments are given in Table 1.

Using this method, the degradation efficiency or conversion (X) of carbendazim with respect to its initial concentration at

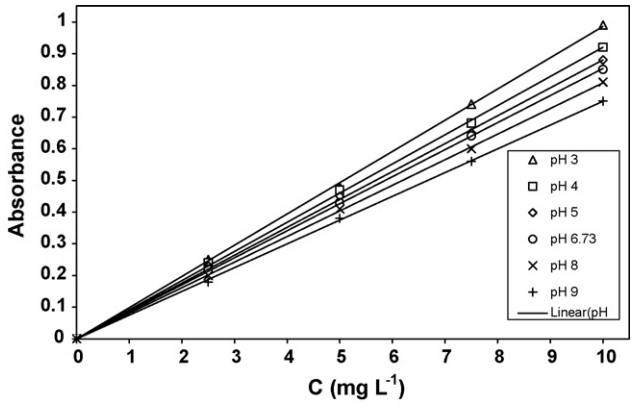

Fig. 2. The calibration chart for measuring carbendazim concentration at different pH values, $T = 25\,^{\circ}C$.

Table 1
The operative conditions of experiments

Parameter	Value
Carbendazim initial concentration	Up to 10 mg L^{-1}
TiO_2 amount	0–90 mg L^{-1}
pH	3–9
Temperature	15–45 °C
Irradiation time	Up to 90 min

any time can be obtained by:

$$X = \frac{C_0 - C}{C_0} \quad (1)$$

where C_0 and C are its initial and concentration at a given time.

2.4. Bioassay evaluation procedure

The toxicological assessment was performed for samples, obtained at different times of photo-degradation, in order to monitor the effectiveness of the degradation process. For this purpose, the extent of mineralization of the fungicide was studied by measuring the mycelium growth inhibition of *Fusarium oxysporum* fungus on PDA medium (Merck product). The *F. oxysporum* is a convenient aquatic test organism in bioassay evaluations and also a suitable fungus in this investigation, since carbendazim is the most effective fungicide in inhibiting mycelium growth of it [19]. PDA medium was prepared by adding 39 g in one liter of de-ionized water and dissolving by stirring on a magnetic hot plate.

Mycelium plugs of six-day old cultures of *F. oxysporum* isolates with 0.3 cm diameter were used to inoculate 6 replicate plates for each isolate. The plates were then incubated under dark conditions at 22 °C. Two alternative incubation times of three and five days were considered [19] and the colony diameters in different directions were measured. Mycelium growth rate (in cm^2/day) in the plates were calculated using the equation:

$$R = \pi \frac{D^2 - d^2}{4t} \quad (2)$$

where D is the average diameter of colony; d initial diameter of fungus medium (0.3 cm) and t incubation time (day). A reference sample with no fungicide in its contain was also used and as a criterion of the toxicity, the percentage of ratio of the mycelium growth rate, $100(R_S/R_M)$, was used; where R_S and R_M are the mycelium growth rates corresponding to the actual samples at a given time and to the reference sample, respectively. Whenever a sample does not contain toxic compounds, a toxicity behavior like the reference sample is expected.

3. Results and discussion

3.1. UV–vis spectra changes

In a precedent study, the absorption spectra of carbendazim were studied at different times of irradiation. As it is presented in Fig. 3, the bands relating to different molecular parts in this fungicide are decreased significantly with respect to time. The obtained spectra show the strong distinctive absorbance peaks at about 282 nm wavelength. The absorbance peaks at around this wavelength are attributed to benzene ring [18]. It has been described that hydroxyl radicals can attack to the aromatic rings [20]. The free-radical reactions are not selective; however, rearrangement of radical intermediates does occur and produces structural fragments. The important fragment in these reactions is aryl radical group which can be decomposed after radicalizing [21]. The nearly perfect disappearance of the band at 282 nm therefore reveals that the aryl group of carbendazim is eliminated in the presence of TiO_2 suspension.

3.2. The influence of TiO_2 particles

The effect of the amount of TiO_2 on degradation of carbendazim is shown in Fig. 4. The photo-degradation efficiency increases with increase in the amount of photocatalyst until about 70 mg L^{-1} of the catalyst and then decreases mildly.

The reason of this observation is thought to be the fact that increasing the concentration of the catalyst cause an increase in the reaction rate, not only because of an increase of the active site of the catalyst but also because of an increase in the hydroxyl rad-

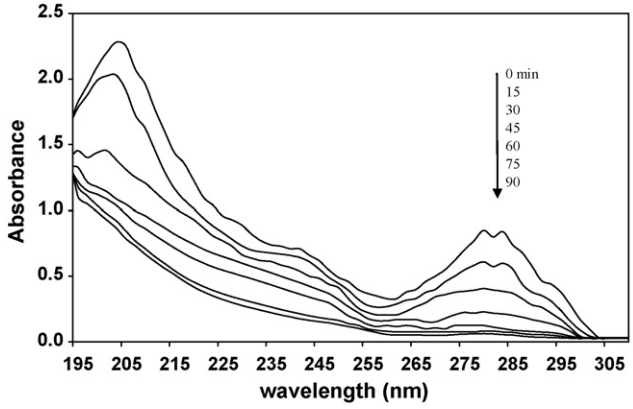

Fig. 3. UV–vis spectra changes of carbendazim at different irradiation times. $[TiO_2] = 70$ mg L^{-1}, pH 6.73 (natural), $T = 25\,^{\circ}C$.

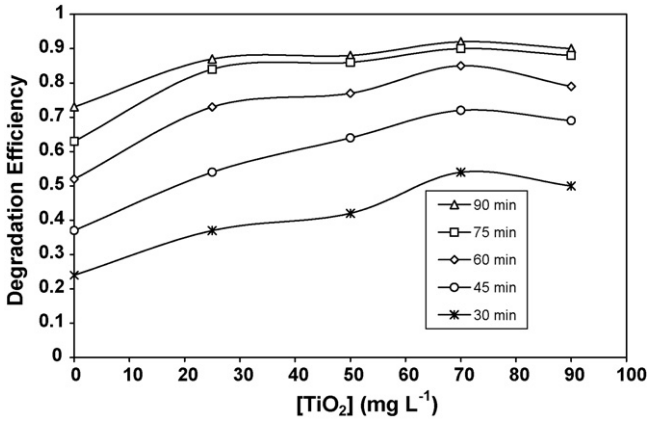

Fig. 4. Effect of the amount of TiO_2 on degradation of carbendazim at different irradiation times. pH 6.73 (natural), $T = 25\,^{\circ}C$.

ical generation; however, on the other hand, when enough TiO_2 is present in the suspension for adsorbing fungicide molecules, the additional higher quantities of it would not have more effect on the degradation efficiency. On the other hand, an increased opacity of the suspension brought about as a result of excess of TiO_2 particles [16].

3.3. Effect of pH

pH is one of the factors influencing the rate of degradation of some organic compounds in the photocatalytic process. It is also an important operational parameter in wastewater treatments. Fig. 5 demonstrates the photocatalytic degradation of carbendazim at different pH values. The most appropriate significant variation is within the pH range of 3–4.

Since pH 3 is significantly less than pK_a (=4.5) of carbendazim in aqueous solution [14], It can be explained by the fact that the protonation takes place and the protonated products are more stable under UV-radiation than its main structure [8]. On the other hand, due to the zero point of charge of TiO_2 (6.25), the catalyst surface is also positively charged [22] leading to a lower level of degradation at pH 3. At pH 4, on the other hand, there will be significantly higher molecules in their non-protonated form, providing higher level of adsorption into catalyst surface and then degradation to be favored.

It should be mentioned that the formation of hydroxyl radicals in acidic solutions and in the presence of oxygen, assists the degradation of substrate as it can be inferred from the following reactions [23]:

$$e^-_{CB} + O_{2(ads)} \rightarrow {}^{-\bullet}O_{2(ads)} \quad (3)$$

$${}^{-\bullet}O_{2(ads)} + H^+ \rightarrow HO_2{}^{\bullet} \quad (4)$$

$$2HO_2{}^{\bullet} \rightarrow O_2 + H_2O_2 \quad (5)$$

$$H_2O_2 + {}^{-\bullet}O_2 \rightarrow {}^{\bullet}OH + OH^- + O_2 \quad (6)$$

Meanwhile, the acceptance of electron by the dissolved oxygen decreases the recombination of recombination of valance band hole (h^+_{VB}) and conduction band electron (e^-_{CB}).

An increase in degradation efficiency from natural pH to 9 could be commented by the significant abundance of OH^- ion in the medium and near the surface of the catalyst that leads to the generation of hydroxyl radicals (the sequential formulas are given in Section 3.5) which has an important role in the degradation. A general increase in only photo-degradation rate of carbendazim with pH has already been reported [8].

To study the influence of substrate adsorption on the catalyst particles surface, a series of experiments were carried out while the UV light was absent. Fig. 6 presents the data for this case. Comparison between this figure with Fig. 5 indicates clearly that the amount of substrate adsorption in the darkness is very low ($X < 0.01$). Meanwhile, the variations show that adsorption under natural pH is relatively higher than the others. In the acidic media, the catalyst surface is positively charged. As the pH of solution decreases, the ratio of neutral form of carbendazim concentration to its protonated form [14] reduces significantly (a ratio of about 0.3 for pH 4 to about 0.03 for pH 3 with respect to its pK_a), providing a low chance of adsorption onto the catalyst surface. On the other hand, in the alkaline media

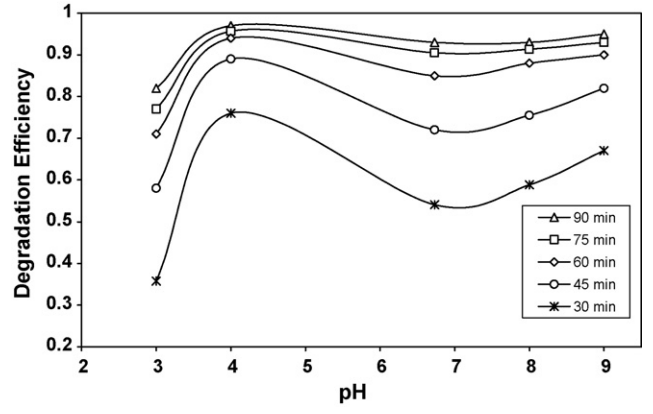

Fig. 5. Effect of pH on degradation of carbendazim at different irradiation times. $[TiO_2] = 70\,mg\,L^{-1}$, $T = 25\,^{\circ}C$.

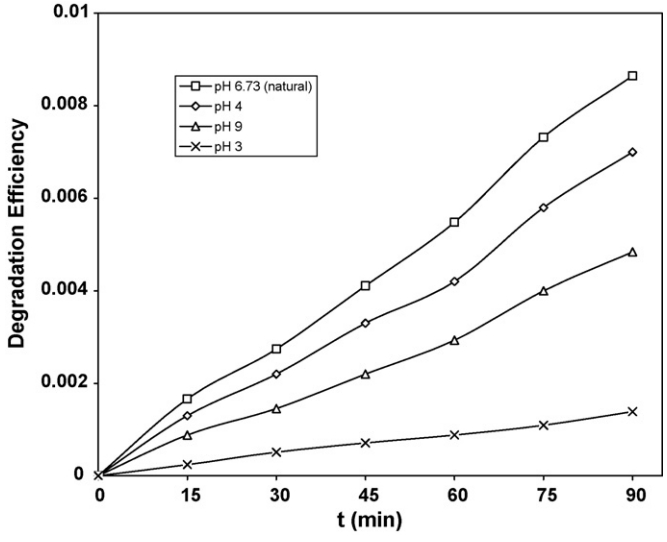

Fig. 6. Darkness adsorption of carbendazim onto the catalyst particles at different pH values. $[TiO_2] = 70\,mg\,L^{-1}$, pH 6.73 (natural), $T = 25\,^{\circ}C$.

the catalyst surface is negatively charged. The carbendazim molecules lose the proton under this condition, consequently form 2-aminobenzimidazole product with a high electron density [8], and hence low tendency to be adsorbed onto the catalyst surface.

Because the difference between carbendazim degradation efficiency under pH 4 and under its natural pH 6.73 after 75 min amounts to only about 6%, the natural pH was chosen as a moderate and optimum pH value and the experiments was followed under this pH, having the advantage that it does not require addition of extra agents to regulate the pH of solution.

3.4. Effect of temperature

In the range of 15–45 °C, a low average enhancement (about 7%) for times up to 75 min in the carbendazim degradation efficiency was observed which must be due to the low activation energy of photocatalytic reaction [24,25]. The photocatalysis with TiO_2 is not therefore, very temperature dependent in this case; however, an increase in temperature helps the reaction to compete more efficiency with the recombination of valance band hole (h^+_{VB}) and conduction band electron (e^-_{CB}). On the other hand, an increase in temperature decreases the solubility of oxygen in water which is not desirable. Temperatures higher than 45 °C will cause significant evaporation of the solution during the experiments.

Since the difference between the degradation efficiency of carbendazim in the temperature range of 25–45 °C after 75 min irradiation amounts to only about 4%, the ambient temperature (25 °C) was chosen as the most suitable temperature value without the need to regulate the temperature.

3.5. Applying the optimum conditions

Fig. 7 demonstrates the photocatalytic degradation of carbendazim under optimum conditions (TiO_2 concentration of 70 mg L^{-1}, pH value of 6.73 and temperature of 25 °C). As it is obvious, more than 90% of substrate degrades in an irradiation time of 75 min, for instance. The only UV-irradiation was also examined while applying the same operating conditions. As presented in Fig. 7, the efficiency of degradation decreases to about 63% after 75 min irradiation. These results show that carbendazim is significantly degraded under UV light when assisted with TiO_2 particles; however, UV light alone is efficient for this degradation.

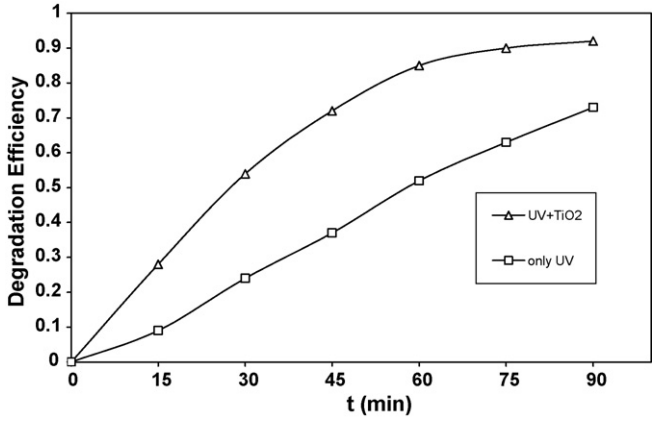

Fig. 7. Effect of TiO_2 particles on degradation of carbendazim at different conditions. [TiO_2] = 70 mg L^{-1}, pH 6.73 (natural), T = 25 °C.

The more activity of the UV/TiO_2 process is due to the well known fact that when TiO_2 is illuminated with the light having $\lambda < 390$ nm, electrons are promoted from the valance band to the conduction band of the semiconducting oxide to give electron–hole pairs. The valance band (h^+_{VB}) potential is positive enough to generate hydroxyl radicals at the surface and the conduction band (e^-_{CB}) is negative enough to reduce the oxygen molecules, present in the solution. The generated hydroxyl radicals are powerful oxidizing agents and attack organic pollutants, present at the surface of TiO_2 or near it (within 0–500 μm) and of course the reaction rate of hydroxyl radicals with pollutants decreases as the distance from surface increases [26]. These cause the degradation of carbendazim according to the following reactions [26,27]:

$$TiO_2 + h\upsilon \rightarrow TiO_2\,(e^-_{CB} + h^+_{VB}) \quad (7)$$

$$h^+_{VB} + e^-_{CB} \rightarrow \text{heat (recombination)} \quad (8)$$

$$h^+_{VB} + H_2O_{(ads)} \rightarrow H^+ + {}^{\bullet}OH_{(ads)} \quad (9)$$

$$h^+_{VB} + OH^-_{(ads)} \rightarrow {}^{\bullet}OH_{(ads)} \quad (10)$$

$$e^-_{CB} + O_{2(ads)} \rightarrow {}^{-\bullet}O_{2(ads)} \quad (11)$$

$${}^{\bullet}OH_{(ads)} + \text{carbendazim} \rightarrow \text{degradationofcarbendazim} \quad (12)$$

$$h^+_{VB} + \text{carbendazim} \rightarrow \text{oxidation of carbendazim} \quad (13)$$

With respect to the significant degradation of carbendazim which was followed by the UV absorbance at appropriate maximum wavelengths, attributed to the benzene ring, and with respect to the reported works on mineralization of other pesticides [28], the appropriate mineralization reaction can be given here with the most oxidized state as:

$$C_9H_9N_3O_2 + 14O_2 \rightarrow 3HNO_3 + 9CO_2 + 3H_2O \quad (14)$$

Recently, the pathways and by-products evaluation of photocatalytic degradation of this fungicide on nano TiO_2 particles have been studied, using a solar light simulating lamp (1500 W) [29].

It should be remarked that nitrogen released have very often been measured as a combination of ammonia and nitrate, but ammonia is oxidized to nitrate after long irradiation times [30]. Of course, the fate of nitrogen strongly depends on its initial oxidation degree. When present in −f3 state, as in amino groups and in our molecule, nitrogen spontaneously evolves as NH_4^+ cation with the same oxidation degree, before being subsequently oxidized into nitrate [31].

3.6. Kinetic studies

Due to the practical applications, the degradation kinetics of carbendazim was investigated under the mild optimum conditions.

In general, according to a great number of investigations, the dependence of the photocatalytic degradation rates on the concentration of organic pollutants has been described well by the Langmuir–Hinshelwood (L–H) kinetic model. The modified L–H equation is given by:

$$r = -\frac{dC}{dt} = k_r\theta = \frac{k_r KC}{1 + KC} \quad (15)$$

where k_r is the reaction rate constant, K the reactant adsorption constant, θ the fraction of TiO_2 surface coverage and C the substrate concentration at any time t.

During photocatalytic degradation, intermediates are formed and may interfere in the determination of kinetics because of competitive adsorption and degradation. Therefore, calculations were done at the beginning of irradiation conversion. During a short time interval, any changes such as intermediates effects could be considered as negligible. The photocatalytic degradation rate can be expressed as a function of concentration according to:

$$r_0 = \frac{k_r KC_0}{1 + KC_0} \quad (16)$$

where r_0 is the initial rate of photocatalytic degradation of carbendazim and C_0 the initial concentration. When the substrate concentration is low enough (less than 10 mg L^{-1} in this work) and there is no catalyst saturation, photocatalytic disappearance with TiO_2, can follow apparent first-order kinetics. In this case, Eq. (16) can be simplified to an apparent first-order kinetic model [32]:

$$\ln\left(\frac{C_0}{C}\right) = k_r Kt = k_{app}t \quad (17)$$

where $k_{app} = k_r K$.

The plot of $\ln(C_0/C)$ versus time in Fig. 8 represents straight lines, from which the slope of linear variations equals to the apparent first-order rate constant, k_{app}. The values corresponding to different initial concentrations, along with the regression coefficients are listed in Table 2. According to the above description, the lower carbandazim concentrations provide the better agreement with the first-order reaction; however, this analysis indicates that concentrations below 10 mg L^{-1} provide satisfactory agreements.

Table 2
Pseudo-first-order apparent constant values for the initial rates of carbendazim degradation

C_0 (mg L^{-1})	$k_{app} \times 10^2$ (min^{-1})	R^2
1	6.89	0.9988
2	5.91	0.9997
5	4.23	0.9962
7.5	3.46	0.9958
10	3.01	0.9908

The influence of the initial concentration of carbendazim on the initial rate of photocatalytic degradation of carbendazim is shown in Fig. 9. The rate of degradation increases with the initial concentration of carbendazim to about 10 mg L^{-1} and then finds a tendency toward independent values with the higher initial concentrations.

The inverse of Eq. (16) in the following expression, gives the dependence of $1/r_0$ values on the appropriate $1/C_0$ values of carbendazim concentration:

$$\frac{1}{r_0} = \frac{1}{k_r} + \frac{1}{k_r K}\frac{1}{C_0} \quad (18)$$

The plot of $1/r_0$ versus $1/C_0$ represented in Fig. 10 shows a linear variation, confirming the Langmuir–Hinshelwood relationship for the initial rates of degradation. The values of k_r and K, calculated from the intercept and the slope of the straight line ($R^2 = 0.9997$) were 0.455 mg L^{-1} min^{-1} and 0.178 L mg^{-1}, respectively.

3.7. Toxicity studies

The photocatalytic reaction process is usually monitored by observing the concentration of the targeted pollutants. Nevertheless, the reduction of pollution is not always accompanied by reduced toxicity. Incomplete degradation and formation of intermediary substances may lead to increased toxicity [33].

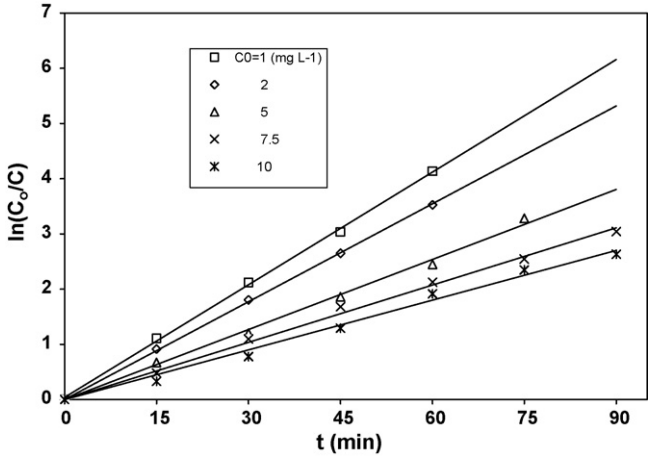

Fig. 8. Linear variation of $\ln(C_0/C)$ versus time of the photocatalytic degradation of carbendazim. $[TiO_2] = 70$ mg L^{-1}, pH 6.73 (natural), $T = 25$ °C.

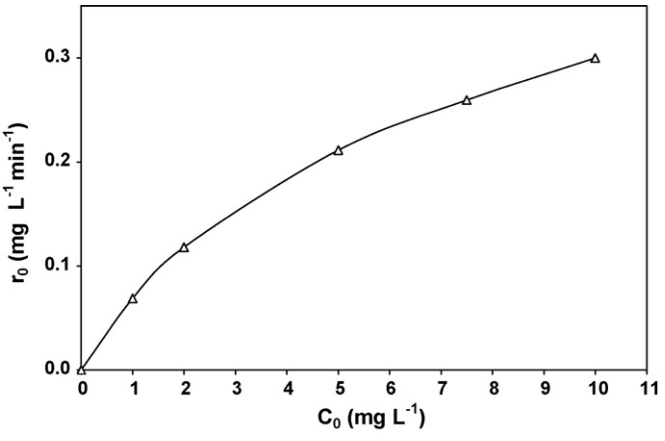

Fig. 9. Variation of initial rate of carbendazim degradation versus different initial concentrations. $[TiO_2] = 70$ mg L^{-1}, pH 6.73 (natural), $T = 25$ °C.

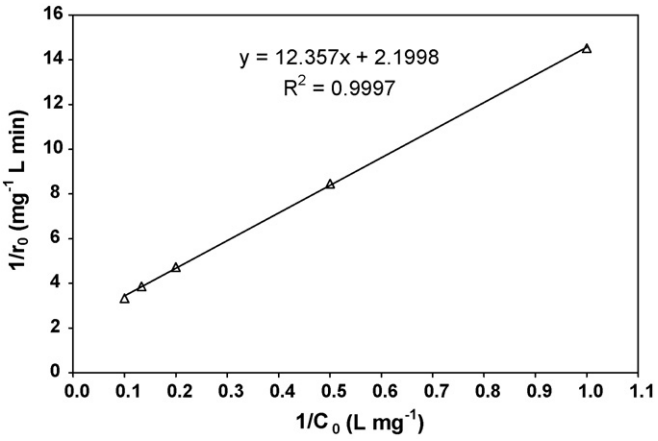

Fig. 10. Variation of parameters in the kinetic model of Eq. (18).

Therefore, it is better that the photocatalytic effect to be evaluated by toxicity estimation using appropriate methods [34,35]. In this regard, the method of measuring of mycelium growth inhibition of *F. oxysporum* fungus on PDA medium was used (described in Section 2.4).

The results, concerning to three and five days incubation times are shown in Fig. 11. As it is apparent in this figure, the criterion of the percentage of the ratio of the mycelium growth rate corresponding to the actual samples to the reference sample tends to a 100% value, confirming that the toxicity of carbendazim solutions tends to very minor levels (providing similar growth rate as the reference sample). This situation is obtained after about 75 min or even 60 min of irradiation. Due to very minor remained fungicide concentration (less than 1 mg L^{-1}) the toxicity was not detected by mycelium growth for samples with more than 75 min of irradiation.

Comparison between results in Figs. 7 and 11 indicates that the kinetics of substrate degradation and toxicity are in reasonably good agreement; however, the toxicity appears to be a slower process during shorter times of irradiation, less than 45 min. This could be due to the formation of some intermediate products, produced during decomposition [2] during this period.

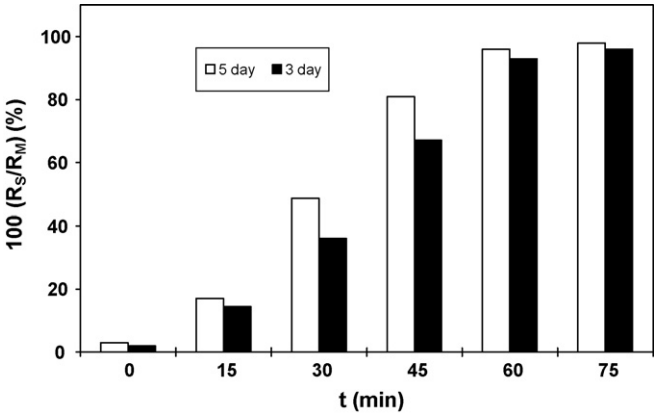

Fig. 11. Evaluation of toxicity of processed carbendazim samples at different irradiation times under optimum conditions, on the mycelium growth of *Fusarium oxysporum* fungus.

4. Conclusions

Effective photocatalytic degradation of the fungicide carbendazim is available in TiO_2 catalyst suspended aqueous solutions and during short times of UV-irradiation when compared with only photo-degradation process.

The results indicate that there is an optimum concentration of suspended TiO_2 catalyst at which the highest degradation efficiency for 10 mg L^{-1} of carbendazim will be available; however, this degradation is not significantly affected by temperature. With the aim of the most degradation, the moderate and the suitable conditions are: catalyst concentration: 70 mg L^{-1}, pH 6.73 (natural pH) and ambient temperature, 25 °C. Under these conditions, for an efficiency of more than 90% of substrate, about 75 min irradiation time is required. The adsorption of substrate on the catalyst particles is not significant compared with those decomposed under photocatalytic degradation.

The Lagnmuir–Hinshelwood kinetic model showed a good agreement for the initial rates of degradation with the appropriate reaction rate constant and the substrate adsorption constant values of 0.455 mg L^{-1} min^{-1} and 0.178 L mg^{-1}, respectively.

Toxicity studies with results obtained by bioassay evaluation, confirmed the effectiveness of the process mainly for irradiation times more than 60 min when the percentage of ratio of the rate of mycelium growth to that of an inert reference sample reaches to more than 95%. Incomplete degradation and formation of intermediary substances may be the reason for the higher level of toxicity compared with the level of degradation at relatively short times of irradiation, less than 45 min.

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