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The influence of polychromatic light on methomyl degradation in TiO_2 and ZnO aqueous suspension

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ABSTRACT

The photocatalytic degradation of the insecticide methomyl in water using TiO_2 Merck Eusolex® T (anatase) under Osram ultra-vitalux® lamp light (315–400 nm, 300 W) was studied. The effect of the operational parameters, such as initial concentration of catalyst, initial methomyl concentration, initial salt concentration (NaCl), and pH, was studied. The optimal concentration of catalyst was found to be 2.0 g/L. Using the Langmuir–Hinshelwood mechanism as a base, a pseudo-first-order kinetic model was illustrated and the adsorption equilibrium constant and the rate constant of the surface reaction were calculated ($K_{MT} = 0.079$ L/mg and $k_C = 0.134$ mg/L min, respectively). The photodegradation rate was higher in acidic than in alkaline conditions. The presence of Cl^- ions significantly affected the photodegradation of the pollutant. The rate of photodecomposition of methomyl was measured using UV spectroscopy and high performance liquid chromatography, while its mineralization was followed using ion chromatography and total organic carbon analysis. In addition, several photocatalysts were used: ZnO (Merck), TiO_2 P-25 (Degussa), TiO_2 Merck (anatase), and TiO_2 Merck R-706 (rutile), and were compared with TiO_2 Merck Eusolex® T (anatase).

Keywords: Photocatalytic degradation; Methomyl; Titanium dioxide; Zinc oxide; Water remediation

1. Introduction

The large-scale development of the agrochemical industry induced by an increase in the World population has led to the increased usage of different agrochemicals. As a consequence, their presence in the environment has also dramatically increased. Among them, methomyl (Fig. 1), a broad spectrum insecticide, is very famous and has been applied widely since its introduction in 1966 [1]. Methomyl, IUPAC name: S-methyl *N*-(methylcarbamoyloxy) thioacetimidate belongs to the family of carbamate pesticides and is effective in two ways: (a) as a "contact insecticide," because it kills target insects upon direct contact and (b) as a "systemic insecticide," because of its capability to cause overall "systemic" poisoning in target insects after it is absorbed and transported throughout the pests that feed on treated plants [2]. It is capable of being absorbed by plants without being

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"phytotoxic" or harmful to the plant. According to European Union pesticides regulations (Annex I, Council Directive 91/414/EEC), methomyl will be in use until at least 2019.

Methomyl is a very toxic and hazardous compound and a pollutant of environmental concern because of its high solubility in water (57.9 g/L at 25˚C) [3]. Its mode of action is by reversible inhibition of acetyl cholinesterase, an essential enzyme for proper functioning of the nervous system. It is noncumulative and rapidly metabolized in both plants and animals to substances of lower toxicity. Considering methomyl's toxicity characteristics, it has been concluded that 0.0025 mg/kg body weight per day (acceptable daily intake, ADI) will not cause adverse effects in humans [4].

After application, methomyl will remain, to some extent, in agricultural soils. Under normal environmental conditions, the pesticide undergoes microbial degradation to carbon dioxide in the soil (Fig. 1).

Neither hydrolysis, nor photolysis is expected to contribute significantly to the degradation of methomyl in water. Methomyl is not readily biodegradable and is relatively stable to hydrolysis under neutral and acidic conditions but has a hydrolysis DT_{50} value of 36 days at pH 9.0 and temperature of 25˚C. Soil adsorption of methomyl is low with a soil adsorption coefficient (Koc) of 13.3–42.8 cm^3/g [4]. Methomyl's low Koc value, high water solubility, and long hydrolysis DT_{50} value indicate that it could be potentially carried by field runoff into surface water. Methomyl has been detected in surface and ground waters across Europe and USA not only during actual application, but also after a long period of use [5].

Although biological processes are often the most economical for contaminated site cleanup and industrial waste treatment, advanced oxidation processes (AOPs) provide an effective means of rapidly treating compounds with efficient process control [6–9]. Among the AOPs, heterogeneous TiO_2 photocatalysis is as an emerging destructive technology leading to the total mineralization of many organic pollutants [6,10–13].

AOPs have also been used for the photodegradation of methomyl: TiO_2 has mostly been used as a catalyst [13–18]. The photo-Fenton reaction has also been investigated [18–24]. The aim of the present work is to study the photocatalytic degradation of insecticide methomyl in deionized water using TiO_2 (Merck Eusolex® T) under the Osram ultra-vitalux® lamp as the light source. The effect of parameters such as the initial concentration of catalyst, initial methomyl concentration, initial salt concentration (NaCl), and pH was studied. The effect of various catalysts, including ZnO, on photodegradation of methomyl was also studied.

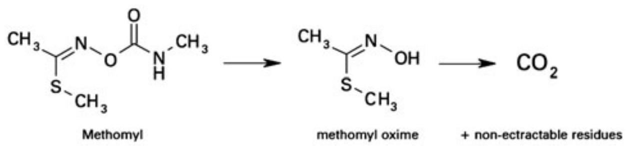

Fig. 1. Degradation pathway of methomyl in soil.

2. Experimental procedure

All the chemicals used in the investigation were of reagent-grade and were used without further purification. HCl, NaOH, NaCl, Na_2CO_3, and $NaHCO_3$ were purchased from Merck. Analytical-grade methomyl (99.8%) was granted by Du Pont De Nemours, USA. TiO_2 (Merck Eusolex® T, anatase modification), TiO_2 P-25 (Degussa), TiO_2 Merck (anatase modification), TiO_2 Merck R-706 (rutile modification), and ZnO (Merck) were used as received. TiO_2 P-25 (Degussa) with 70% anatase and 30% rutile, surface area 50 m^2/g, and particle size 25 nm. TiO_2 Merck (anatase) with a surface area of 10 m^2/g. ZnO (Merck) with surface area 10 m^2/g and particle size 0.1–4.0 μm. The acetonitrile used for high performance liquid chromatography (HPLC) analysis was HPLC-grade and was provided by Fluka. Methanesulfonic acid for ion chromatographic analysis was provided by Fluka. All the solutions were prepared immediately prior to use with Millipore Waters deionized water (18.2 $M\Omega\,cm^{-1}$at 25˚C).

Irradiations under 315–400 nm were performed in a glass reactor (cylindrical shape, volume 30.0 mL) with an Osram ultra-vitalux® lamp (mix of lights; UV-A:UV-B = 13.6:3 according to the manufacturer's specifications) placed 300 mm from the surface of the reaction mixture. The photodegradation of methomyl was studied by preparing a solution containing 16.22 mg/L of methomyl and a certain amount of catalyst. In a typical experiment, 25 mL of solution was used and five samples were investigated for each analysis. Then the lamp was switched on and during the irradiation, agitation was applied. After an appropriate time for irradiation, the suspension was sampled. The reaction mixtures were kept at 20.0 ± 0.1˚C. The concentration of methomyl was determined (after centrifugation of a sample) by UV–vis spectrophotometer (Shimadzu 1700) at $\lambda_{max} = 233.8$ nm and HPLC. The characteristics of the HPLC instrument are as follows: Hewlett Packard HP 1050 with a UV–vis detector, column Zorbax 150 × 4.6 mm (i.d.) × 5 μm, the mobile phase acetonitrile:water (25:75, flow rate

2.0 mL/min), and wavelength 234 nm. The sample injection volume was 20 μL, and both samples and standards were diluted with acetonitrile. The pH of the samples was adjusted by adding NaOH or HCl solution and measured using a pH meter (pH meter Inolab pH 730, Germany). The concentration of ions was monitored by a Dionex DX-300 ion chromatograph at ambient temperature (25°C) with a suppressed conductivity detector. For total organic carbon (TOC) analysis, the samples were analyzed on a Zellweger LabTOC 2100 instrument using high-temperature combustion followed by infra-red CO_2 detection.

3. Results and discussion

3.1. UV–vis spectra changes

Fig. 2 presents changes in the absorption spectra of the methomyl solution during photocatalytic degradation in the presence of TiO_2 Merck Eusolex® T (anatase) at different irradiation times. The insecticide shows a band with a maximum absorption at 234 nm. The decrease of the absorption peak actually indicates the rapid degradation of insecticide. No change in the concentration was observed when the catalyst was used in the absence of light. In addition, a small, almost nonexistent, change in the concentration was observed when only light was applied. HPLC analysis confirmed the disappearance of methomyl and was in agreement with the UV analysis.

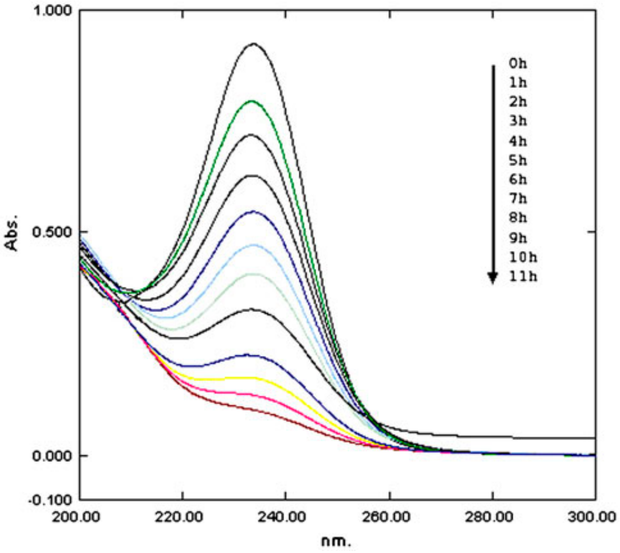

Fig. 2. UV–vis spectra changes of methomyl (16.22 mg/L) in 1.0 g/L aqueous TiO_2 (Merck Eusolex® T) dispersion irradiated with Osram Ultra vitalux® lamp.

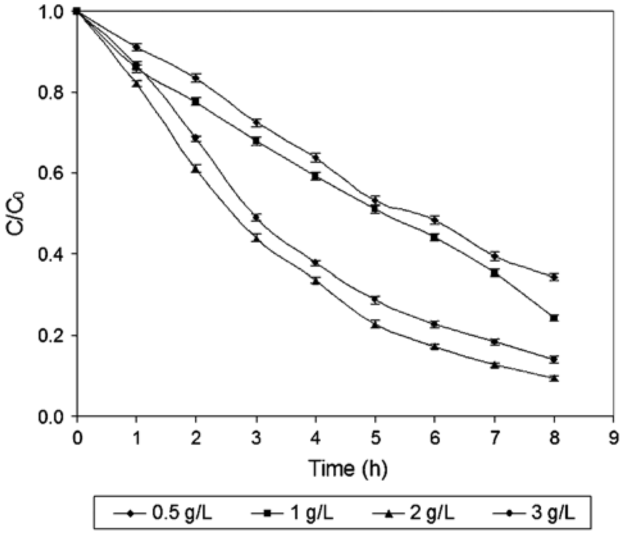

Fig. 3. The effect of the initial concentration of TiO_2 (Merck Eusolex® T) on the photodegradation of methomyl (methomyl concentration = 16.22 mg/L).

3.2. Effect of the catalyst amount

The degradation curves {normalized concentration (C/C_o, where C is the concentration of methomyl at irradiation time t, and C_o is the initial concentration of methomyl) vs. time} shown in Fig. 3 represent the effect of the TiO_2 (Merck Eusolex® T) concentration on the photodegradation of methomyl.

The kinetics of the photodegradation rate of most organic contaminants [25] can be well described using a pseudo-first-kinetic order, which is given by the following equations:

$$\ln(C_o/C) = k \times t \tag{1}$$

$$C = C_o\, e^{-k\times t} \tag{2}$$

where C_o, C, and t are as given above, k is the pseudo-first-order rate constant. For reactions of pseudo-first-order, the half-time of the reaction can be calculated using:

$$t_{1/2} = \ln 2/k \tag{3}$$

The effect of the TiO_2 (Merck Eusolex® T) concentration on the initial reaction rate is shown in Fig. 4. All the experiments were performed with 0.5, 1.0, 2.0, and 3.0 g/L of TiO_2. The highest reaction rate was observed when 2.0 g/L of TiO_2 was used. Photodegradation efficiency increased as the concentration of the photocatalyst increased reaching the highest value at 2.0 g/L and then decreasing. A possible explanation

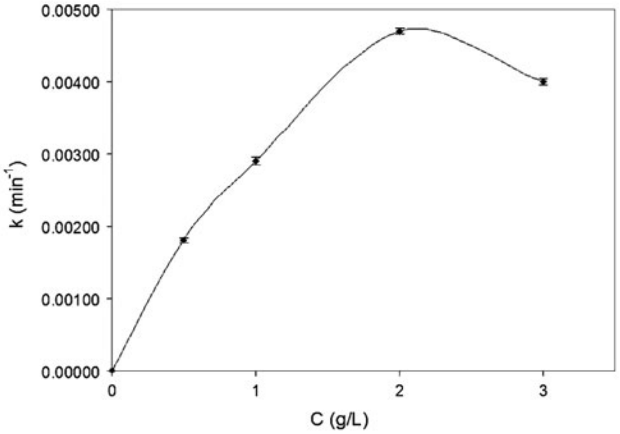

Fig. 4. The effect of the TiO_2 (Merck Eusolex® T) concentration on the methomyl photodegradation rate (methomyl concentration = 16.22 mg/L).

for this phenomenon is that when all insecticide molecules are adsorbed by TiO_2, the addition of higher quantities of TiO_2 has no further effect on photodegradation efficiency. Above this concentration, light scattering [10,12] and coagulation of the catalyst particles decreased the reaction rate [10,12,26,27] and a reduced degradation rate was registered when the concentration of TiO_2 was increased beyond 2.0 g/L.

3.3. Effect of the initial methomyl concentration

In addition, the effect of the initial methomyl concentration on photodegradation was studied and the results obtained are presented in Fig. 5. Using Eqs. 1 and 3, it is possible to calculate the pseudo-first-order constant and half-time of the reaction when different initial concentrations of methomyl were used. The results given in Table 1 show that an increase in the initial methomyl concentration leads to a lower photodegradation rate. Here, by increasing the methomyl concentration, more and more methomyl molecules were adsorbed on the surface of the TiO_2 (Merck Eusolex® T), which contributed to the inhibition of the reaction between methomyl molecules and holes or hydroxyl radicals due to the lack of any direct contact between them [28].

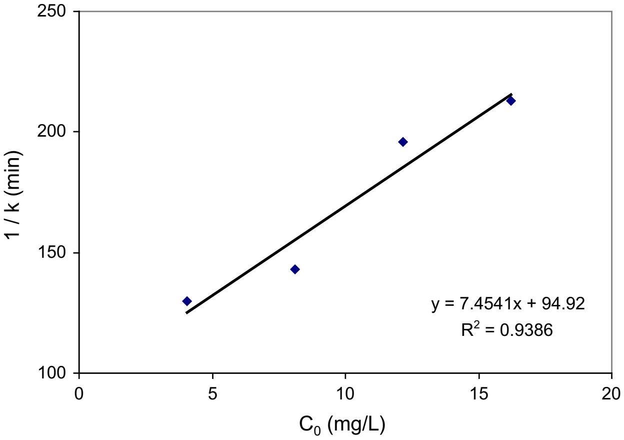

Fig. 5. Linear transformation of the L–H type expression.

A heterogeneous photocatalytic reaction can be successfully analyzed using the modified Langmuir–Hinshelwood (L–H) kinetic expression [25,26,28,29]. The rate of oxidation of methomyl by a surface reaction is proportional to the surface coverage of methomyl on the TiO_2 (Merck Eusolex® T) assuming that methomyl is adsorbed more strongly on the catalyst surface than on the intermediate products. The effect of the initial methomyl concentration C_o on the initial methomyl degradation rate r is given in the form of Eqs. (4) and (5):

$$r = \frac{K_{MT}\, k_C\, C}{1 + K_{MT}\, C_o} = k\,C \tag{4}$$

$$\frac{1}{k} = \frac{1}{K_{MT}\, k_C} + \frac{C_o}{k_C} \tag{5}$$

where K_{MT}, k_C, and k are the Langmuir–Hinshelwood adsorption equilibrium constant, the rate constant of the photodegradation surface reaction, and the rate constant of the initial methomyl photodegradation reaction, respectively. At the investigated concentrations, i.e. concentrations up to 16.22 mg/L, the applicability of the L–H equation for the photocatalytic degradation was confirmed by the linear plot ($R = 0.9686$), obtained by plotting the reciprocal of the rate constant ($1/k$) against the initial concentration. The values of K_{MT} and k_C were found to be 0.079 L/mg and 0.134 mg/L min, respectively.

3.4. Effect of the initial pH

It is known that pH value has an influence on the photodegradation of some organic compounds in photocatalytic processes [10,12,13,23,26,29–32]. The photodegradation of methomyl was studied at four different pH values (2.0, 3.5, 5.6, and 9.0) with a methomyl concentration of 16.22 mg/L using a TiO_2 Merck Eusolex® T concentration of 2 g/L. The third value is the pH of a pure methomyl solution in deionized water. The pH of the solution was adjusted before irradiation (by the addition of HCl or NaOH solutions). The amphoteric behavior of most semiconductor oxides influences the surface charge of the

Table 1
Kinetics of methomyl degradation under Osram ultra-vitalux® lamp (TiO_2 Merck Eusolex® T concentration = 2 g/L)

Co (mg/L)	k (min^{-1})	$1/k$ (min)	R
16.22	0.0047	212.77	0.9998
12.15	0.0051	196.08	0.9851
8.10	0.0070	142.86	0.9771
4.05	0.0077	129.87	0.9620

photocatalyst. According to Ref.[29], the zero point charge for TiO_2 (pHzpc) is 5.0–6.0, and above this value, the TiO_2 surface is predominantly negatively charged (TiO^-) (Eq. (6)). The surface of the catalyst is positive below pH 6.0 and as the pH decreases, the functional groups are protonated ($TiOH_2^+$) and the proportion of the positively charged surface increases (Eq. (7)) [11]:

$$\mathrm{TiOH} + \mathrm{OH}^- \longleftrightarrow \mathrm{TiO}^- + \mathrm{H_2O} \quad \mathrm{pH} > \mathrm{pHzpc} \tag{6}$$

$$\mathrm{TiOH} + \mathrm{H}^+ \longleftrightarrow \mathrm{TiOH}_2^+ \quad \mathrm{pH} < \mathrm{pHzpc} \tag{7}$$

It was found that the initial photodegradation rate decreased as the pH value increased (Fig. 6). Here and in a previous paper [13], it was demonstrated that the photodegradation rate is the highest in the acidic solution and lowest in the alkaline solution, while Tamimi et al. [16] reported that the photodegradation rate of methomyl was the lowest in acidic solution, had a maximum value in the neutral solution, and once more decreased in the alkaline solution.

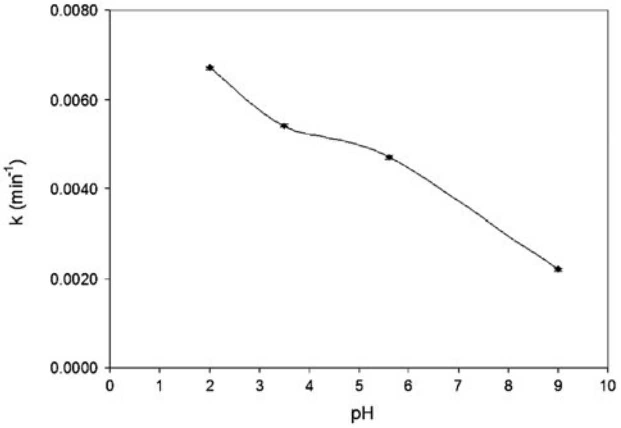

Fig. 6. The effect of pH on the methomyl photodegradation rate (TiO_2 Merck Eusolex® T concentration = 2.0 g/L, methomyl concentration = 16.22 mg/L).

3.5. Effect of the salt concentration

This phenomenon was frequently investigated because of the possibility of adsorption of inorganic anions into the photocatalyst surface. This should result in a decrease in the number of holes and ·OH radicals, and the reaction rate should decrease [26,32]. The presence of different inorganic ions (SO_4^{2-}, HSO_4^-, PO_4^{3-}, CO_3^{2-}, HCO_3^-, Cl^-, NO_3^-, etc), normally present in both surface and ground waters, leads to a decrease in the effectiveness of photodegradation due to its scavenging properties [32].

The effect of salt on the photodegradation of methomyl was studied using sodium chloride. The influence of different concentrations of salt (0.0, 1.0, and 5.0% w/v) is presented in Fig. 7. The observed decrease in the photodegradation of methomyl in the presence of chloride ions can be explained by competitive adsorption [32,33] or by the hole-scavenging properties of chloride ions [32,34]:

$$\mathrm{Cl}^- + h_{\mathrm{VB}}^+ \rightarrow \mathrm{Cl}^{\cdot} \tag{8}$$

$$\mathrm{Cl}^{\cdot} + \mathrm{Cl}^- \rightarrow \mathrm{Cl}_2^{-\cdot} \tag{9}$$

$$\mathrm{OH}^{\cdot} + \mathrm{Cl}^- \rightarrow \mathrm{Cl}^{\cdot} + \mathrm{OH}^- \tag{10}$$

This is an example of competitive inhibition between the pesticide molecule and the Cl^- ions. While chlorine radicals are formed slowly, they are converted into chloride anions instantly. The surface sites normally available at the TiO_2/methomyl solu-

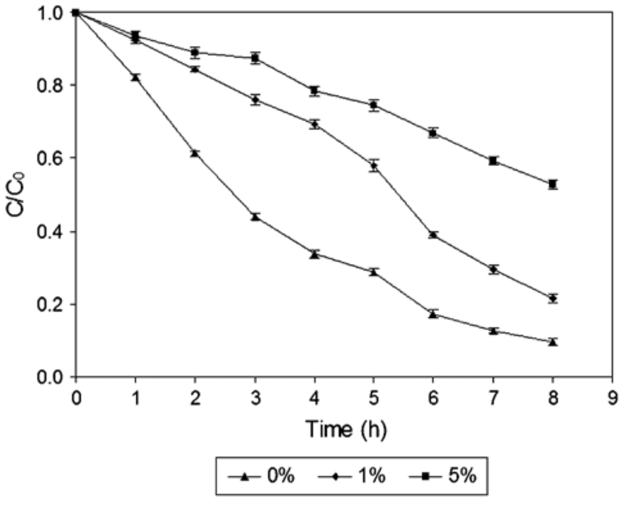

Fig. 7. The effect of the NaCl concentration on the photodegradation of methomyl (methomyl concentration = 16.22 mg/L, TiO_2 Merck Eusolex® T concentration = 2.0 g/L).

tion interface for adsorption and electron transfer from methomyl can be blocked by anions, such as chloride anions, which are not oxidizable and are effective inhibitors of the detoxification process [32]. Our results are in accordance with Tamimi et al. [16], who also reported that the presence of NaCl led to inhibition of methomyl photocatalytic process.

3.6. Effect of the ZnO

In the second part of the experimental work, the influence of ZnO (Merck) on the reaction rate of methomyl photodegradation was studied and compared with TiO_2 (Merck Eusolex® T, anatase) (Fig. 8). Because the TiO_2 reaction proceeded fastest when 2.0 g/L of TiO_2 was used, experiments with ZnO were performed with the same concentration. Fig. 8 shows that the photodegradation of methomyl was much faster when ZnO was used ($k = 0.0100\ min^{-1}$, $t_{1/2} = 69.31$ min) than when TiO_2 was used ($k = 0.0047\ min^{-1}$, $t_{1/2} = 147.48$ min). The most important advantage of ZnO over TiO_2 is that it absorbs over a larger fraction of the UV spectrum: the corresponding threshold wavelength of ZnO is 425 nm [26] relative to 440 nm [35]. In spite of our results, many researchers believe that TiO_2 is a better catalyst than ZnO because TiO_2 is more stable during the photocatalytic reaction [25].

3.7. Mineralization study of methomyl

The target of each photocatalytic process is the complete mineralization of contaminants. In our experimental work, two types of semiconductor catalyst were used: TiO_2 (Merck Eusolex® T) and ZnO (Merck), both in concentration of 2 g/L. The ion chromatography (IC) results showed that mineralization led to the formation of sulfate, nitrate, and ammonium ions during the process (Table 2) while Tamimi et al. [17] reported the formation of only sulfate and ammonium ions. In our experiments, the mineralization of sulfur atoms into sulfate ions was almost complete and the maximum expected value for sulfate ions (around 9.60 mg/L) was obtained. It is also known that in photocatalytic oxidation, the extreme oxidation state of nitrogen depends on the nature and concentration of the substrate, also on the reaction conditions [14]. The maximum detected values for nitrate and ammonium ions were 1.05 and 1.09 mg/L, respectively. The nitrogen mass balance was therefore incomplete at the end of the treatment (around 50% of the inorganic nitrogen expected in the process). In the presence of TiO_2, mineralization of organic carbon was incomplete and about 80% of initial TOC disappeared after 8 h. In the presence of ZnO, however, about 80% of initial TOC disappeared after only 4 h. Our results are in accordance with the results of Oller et al. [18], who also reported that in the methomyl mineralization process SO_4^{2-}, NO_3^-, and NH_4^+ ions

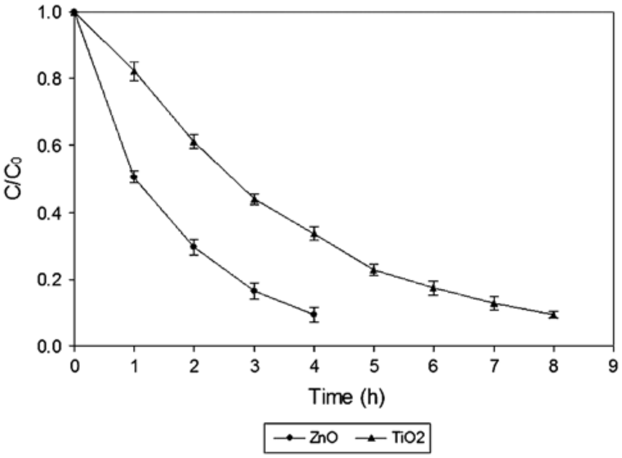

Fig. 8. The effect of the catalyst type on the photocatalytic removal rate of methomyl (catalyst concentration = 2.0 g/L, methomyl concentration = 16.22 mg/L).

Table 2
Mineralization of methomyl under Osram ultra-vitalux® lamp (catalyst concentration = 2 g/L)

Time (h)	Parameter (mg/L)	315–400 nm	
		TiO_2	ZnO
0	SO_4^{2-}	0.000 ± 0.000	0.000 ± 0.000
	NO_3^-	0.000 ± 0.000	0.000 ± 0.000
	NH_4^+	0.000 ± 0.000	0.000 ± 0.000
	TOC	6.000 ± 0.190	6.000 ± 0.190
2	SO_4^{2-}	2.930 ± 0.042	5.810 ± 0.084
	NO_3^-	0.250 ± 0.003	0.320 ± 0.004
	NH_4^+	0.470 ± 0.001	0.580 ± 0.001
	TOC	5.530 ± 0.190	3.340 ± 0.190
4	SO_4^{2-}	5.280 ± 0.076	9.280 ± 0.135
	NO_3^-	0.530 ± 0.006	0.710 ± 0.008
	NH_4^+	0.710 ± 0.001	1.020 ± 0.002
	TOC	4.050 ± 0.190	1.250 ± 0.190
6	SO_4^{2-}	7.430 ± 0.108	
	NO_3^-	0.790 ± 0.009	
	NH_4^+	0.900 ± 0.002	
	TOC	2.300 ± 0.190	
8	SO_4^{2-}	9.220 ± 0.134	
	NO_3^-	1.050 ± 0.013	
	NH_4^+	1.090 ± 0.002	
	TOC	1.350 ± 0.190	

were formed. All the sulphur from the methomyl molecule was converted into sulfate ions and only 43% of the initial nitrogen from the methomyl molecule was converted into NO_3^- and NH_4^+ ions. Also, our results are in relative accordance with Poulios et al. [14], who reported the presence of NH_4^+ and NO_3^- ions (around 90% of the inorganic nitrogen expected in the process) and 100% conversion of sulfur into SO_4^{2-} ions (when ZnO was used), and with Fernández–Alba et al. [19], who presented the formation of only SO_4^{2-} and NH_4^+ ions, both in the stehiometric relation, during solar TiO_2 Degussa P-25 methomyl degradation.

3.8. Effect of TiO_2 catalyst type

In the third part of the experimental work, the influence of TiO_2 catalyst type (P-25 Degussa, Merck anatase, and Merck R-706 rutile) on the reaction rate of methomyl catalysis was studied and compared with TiO_2 Merck Eusolex® T, anatase (Table 3). In all cases, the dissipation of methomyl followed a pseudo-first-kinetic order. Table 3 shows that the photodegradation of methomyl was much faster when TiO_2 P-25 Degussa was used ($k = 0.0151\,\text{min}^{-1}$, $t_{1/2} = 45.90\,\text{min}$). When P-25 (Degussa) was used, the rate constant of methomyl was 2.2 times faster than in the presence of Merck (anatase) ($k = 0.0069\,\text{min}^{-1}$) and was three times faster than in the presence of Merck Eusolex® T anatase ($k = 0.0047\,\text{min}^{-1}$). In the presence of Merck R-706 (rutile), methomyl photodegraded approximately 17 times slower ($t_{1/2=}770.16$ min) than in the presence of P-25 Degussa.

Anatase and rutile are two of the most famous modifications of the semiconductor TiO_2, and it is known that in photocatalytic processes, the anatase modification is more effective than the rutile modification [36]. Photocatalyst TiO_2 P-25 (Degussa), which consists of anatase and rutile modifications in the relation 3:1, is highly efficient because of their synergistic effect (anatase is a carrier for rutile). The authors [37,38], reported that P-25 (Degussa) owes its high photoreactivity to a slower recombination between electrons and holes. Also, according to Ref.[39], P-25 (Degussa) has higher photocatalytic activity than the other commercial types of TiO_2.

Table 3
Kinetics of methomyl degradation under Osram ultra-vitalux lamp with 2 g/L of catalyst

TiO_2 type	k (min^{-1})	R	$t_{1/2}$ (min)
P-25 (Degussa)	0.0151	0.9918	45.90
Merck (anatase)	0.0069	0.9989	100.46
Merck Eusolex® T (anatase)	0.0047	0.9941	147.48
Merck R-706 (rutile)	0.0009	0.9814	770.16

Our results are in accordance with the results of Poulios et al. [14], who also investigated methomyl photocatalytic degradation in the presence of two types of TiO_2, P-25 Degussa and Hombikat UV-100 (100% anatase), and confirmed that the process was considerably slower in the presence of the Hombikat UV-100 modification. The efficiency of P-25 Degussa related to the Hombikat UV-100 catalyst was explained by crystal morphology, which is one of the most critical parameters of the photocatalytic effectiveness of P-25 related to the other TiO_2 modifications [40].

4. Conclusions

In this study, 315–400 nm of polychromatic light was employed for the efficient purification of a water solution containing 16.22 mg/L of the famous and very hazardous carbamate insecticide methomyl. The reaction rate depended on the initial concentration of the catalyst, initial methomyl concentration, pH, and initial NaCl concentration. The use of 2.0 g/L of TiO_2 Merck Eusolex® T (anatase) gave the best reaction rate. A pseudo-first-order kinetic model was confirmed on the basis of the L–H mechanism. In addition, it was found that the reaction proceeded fastest in an acidic solution, while the presence of Cl^- ions led to its inhibition. Degradation of the insecticide performed in the presence of the same concentration of ZnO (Merck) showed that methomyl photodegraded approximately two times faster in the presence of ZnO than in the presence of TiO_2 Merck Eusolex® T (anatase). Sulfate, nitrate, and ammonium ions were formed during the remediation process, both in the presence of TiO_2 and ZnO. TiO_2 P-25 Degussa was found to be the best catalyst for the photodegradation of methomyl.

Acknowledgments

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