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A STUDY OF PHOTOCATALYTIC DEGRADATION OF METHOMYL AND ITS COMMERCIAL PRODUCT LANNATE-90

Article Highlights

- Photocatalysis of pure methomyl and its commercial product Lannate-90 were investigated
- The kinetics of methomyl and Lannate-90 were studied and pseudo first-order was determined
- Photodegradation of Lannate-90 was much faster than photodegradation of pure methomyl
- TiO₂ is a better catalyst than ZnO for both methomyl and Lannate-90
- Three major transformation products of photocatalytical degradation were identified

Abstract

Photocatalytic degradation of the carbamate insecticide methomyl and its commercial product Lannate-90 in aqueous suspension of TiO₂ and ZnO using an Osram ultra-vitalux lamp (315–400 nm) was investigated. The objective of the investigation was to study and compare the rates of photochemical degradation of the pure active compound and its formulated product in order to find out the impact of inert ingredients on degradation processes. The photochemical degradation of pure methomyl was found to be slower than the degradation of its commercial product Lannate-90. Photodegradation was investigated by UV-Vis spectrometry and HPLC, while mineralization was monitored using IC and TOC analyses. Light absorption capabilities of catalysts were characterized by ultraviolet-visible diffuse reflectance spectroscopy method, while the stability of catalysts was studied by infrared analyses. Degradation products of methomyl and its formulated product were identified by high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) results and tentative photodegradation pathways were proposed.

Keywords: Lannate-90, methomyl, photocatalysis, titanium dioxide, zinc oxide.

Pesticides are a very important class of water pollutants, especially because of their extensive application. There is a great public concern over the potential damage that pesticide residues may cause to the environment. Heterogeneous photocatalytic degradation has been recognized as a useful way for treating water-polluting pesticides [1-6]. Among the various semiconductors employed, TiO₂ and ZnO

were the most studied due to their good photocatalytic properties [2,5]. In order to evaluate TiO₂ and ZnO catalytic properties, optical and morphological characterizations of catalysts were studied [7-12].

To be able to apply pesticides in agriculture correctly, it is necessary to prepare them in forms in which their application is possible. This process is called formulation and it consists of transferring an active pesticide ingredient into a final product. All pesticide formulations are mixtures, always containing the crucial active ingredient(s) and various other inert ingredients, depending of the type of formulation. Those inert ingredients may be: antifoam compounds, surfactants, solvents, antifreeze compounds, stability agents, carriers, dyes (occasionally), etc. [13,14].

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Methomyl (Figure S1, Supplementary Material, available from the author upon request), *S*-methyl-*N*-(methylcarbamoyloxy)thioacetimidate, CAS RN: 16752-77-5, WHO class: Ib, belongs to the group of carbamate pesticides, a large group of pesticides that have been extensively used for many years. Due to their widespread use in agriculture and relatively good solubility in water, carbamate compounds can contaminate both surface and ground waters [15]. Methomyl is found on the market formulated as: soluble concentrate (SL), soluble powder (SP), and wettable powder (WP). The low adsorption coefficient of methomyl (K_{oc} of 13.3–42.8 mL g⁻¹), its high water solubility (57.9 g L⁻¹, 25 °C), and long stability during hydrolysis under neutral and acid water conditions (DT_{50} = 30 days, pH 9, 25 °C) indicate that it could be carried by field runoff into surface water [16,17].

Although photodegradation of pure active ingredients of pesticides has been the subject of many published papers [1,2,4,5,18–21], only several papers focused on the degradation of commercial pesticide products [3,22–25]. The objective of our investigation was to study and compare the rates of photochemical degradation of the pesticide active ingredient methomyl and its commercial product Lannate-90 (soluble powder-SP). The goal was to find out if inert ingredients impact the complex process of photodegradation of the active ingredient. The effect of reaction conditions on methomyl degradation kinetics was investigated. Also, the influence of initial pH on photodegradation of methomyl and its formulated product were monitored and compared. In addition, the optical and morphological characterizations of both catalysts were studied. Furthermore, several different photoproducts of methomyl degradation occurring during this photoprocess were detected and characterized by HPLC-MS. Finally, based on the detected transformation products, degradation pathways of the pesticide, both as pure ingredient and formulated product, were proposed. To the best of our knowledge, there are no other reported studies focusing on this phenomenon.

EXPERIMENTAL

Reagents

Sodium hydroxide, hydrochloric acid, sodium carbonate, sodium hydrogen carbonate, and acetic acid were purchased from Merck. Analytical-grade methomyl (99.8%) was granted by DuPont De Nemours, USA. Lannate-90 was used as a commercial product (DuPont De Nemours, USA). Since the content of commercial pesticide formulations is usually a

secret, the scarce information found about them was collected from safety data sheets and general information on formulations of specific types. Lannate-90 is a water-soluble powder (SP) and contains 895.2 g kg⁻¹ of the active ingredient methomyl (manufacturer's data 900 g kg⁻¹). Soluble powder (SP) is a solid formulation designed to be mixed with water before use. Soluble powders dissolve readily and form a true solution. Typical formulation contents include: an active ingredient (very high content of active ingredient), wetting agent, inert filler, and dye [26–28]. The photocatalysts employed in this experiment were commercial ZnO obtained from Merck with 10 m² g⁻¹ surface area and 0.1–4.0 μm particle size, and TiO₂ P-25 (Degussa) having 70% anatase and 30% rutile, 50 m² g⁻¹ surface area and 25 nm particle size. HPLC-grade acetonitrile and methanol, and methanesulfonic acid for ion chromatographic analysis were provided by Fluka. All solutions were prepared with Millipore Waters deionized water (18.2 MΩ cm⁻¹ at 25 °C) and were prepared immediately prior to use.

Photodegradation procedure

Solutions were prepared by dissolving methomyl and Lannate-90 in deionized water with additional dissolution for 60 min in an ultrasonic water bath. The initial methomyl and Lannate-90 concentrations were 16.2 mg L⁻¹ (1×10⁻⁴ M). The irradiation reactions were performed in an open glass thermostated cylindrical shape reactor (volume 500.0 mL, 20 °C) with an 300 W 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 (Figure S2, available as supplementary material). An amount of 250 mL of methomyl (or Lannate) solution and 2.0 g L⁻¹ of catalyst were added and the mixture was agitated (500 rpm). The adsorption of methomyl onto the catalyst surface was studied for 60 min for both catalysts. Then the lamp was switched on and the irradiation time was 75 and 90 min in the TiO₂ and ZnO experiments, respectively. After each specific time interval, an appropriate sample of the suspension was taken, centrifuged (Rotofix 32, Germany) for 15 min, and filtered through a 0.20 μm Sartorius filter.

Analytical procedure

The UV spectra of both pure methomyl and Lannate-90 were recorded on a Shimadzu 1700 UV-Vis spectrophotometer in a wavelength range of 200–300 nm, while the kinetics of methomyl degradation was monitored at 234.0 nm. For all samples, 3.0 mL of the solution was taken and all UV-Vis analyses were done in triplicate. The HPLC analysis was per-

formed at 234 nm on a Hewlett Packard HP 1050 liquid chromatograph equipped with a UV-Vis detector (details available as supplementary material). Ion chromatography data were obtained on a Dionex DX-300 ion chromatograph. A Zellweger LabTOC 2100 instrument was used in a total organic carbon (TOC) analysis. HPLC-MS/MS analysis was conducted as before [23] using a Thermo Fisher Scientific (Waltham, MA, USA) apparatus (details available as supplementary material).

Infrared analysis

IR spectra were obtained on a Nicolet iS 20 FTIR spectrometer using Everest diamond attenuated total reflectance (ATR) accessory (Thermo Fisher Scientific, Waltham, MA, USA).

The band gap determination

Shimadzu UV-Vis UV-2600 spectrophotometer (Japan) was used for diffuse reflection spectra measurements. The spectrophotometer was equipped with an integrated sphere (ISR-2600 Plus (for UV-2600)). The spectra were obtained in the range from 220 to 900 nm with 1 nm resolution.

The band gap (E_g) was determined [29,30] by using the following equation:

$$(F_{KM}(R)h\nu)^{1/n} = A(h\nu - E_g) \quad (1)$$

where: $F_{KM}(R)$ represents the Kubelka-Munk function, with $F_{KM}(R) = (1-R)^2/2R$, R represents the observed reflectance in the UV/Vis spectrum, A represents the constant and $h\nu$ represents the photon energy (E_{phot}), and extrapolating the linear region of the plot to $(F_{KM}(R)h\nu)^{1/n} = 0$. The values of n are 1/2, 2 and 3/2, for direct allowed, indirect allowed, and direct forbidden transitions, respectively.

Statistical analysis and measurement uncertainty

It is known that heterogeneous photocatalytic degradation depends on more different factors: initial concentration of reactants, type of catalyst, initial concentration of catalyst, pH of solution, irradiation type and intensity, reaction temperature, influence of electron-acceptors, presence of inorganic anions, nature of pollutant, etc. In this work, all important parameters such as initial concentration of pollutants and catalysts, rotational speed of stirrer, reaction temperature, light intensity, as well as initial pH values, were always constant. So, the statistical analysis [31,32] was applied to the concentration change during the experiments. The statistical analysis (standard deviation and relative standard deviation) is available as supplementary Tables S1 and S2. All experiments

were run at least in triplicates. The mean relative standard deviation was less than 3%.

RESULTS AND DISCUSSION

In the first part of the study, the influence of reaction conditions, including the type of catalyst and initial pH, on photodegradation of methomyl and its formulated product Lannate-90 were examined. In the second part of the experiment, mineralization of methomyl (and Lannate-90) in the presence of TiO_2 or ZnO photocatalysts were investigated and photodegradation pathways were proposed.

The effect of reaction conditions on photodegradation

The influence of TiO_2 and ZnO catalyst concentrations on methomyl photodegradation had been evaluated earlier [2,5,33] and the concentration of 2.0 g L^{-1} was again used based on the results of earlier tests. Adsorption and photodegradation curves (normalized concentration (C/C_0 , where C is the concentration of methomyl at irradiation time t and C_0 is the initial concentration of methomyl) vs. time) are shown in Figure 1. Methomyl is known to be stable during

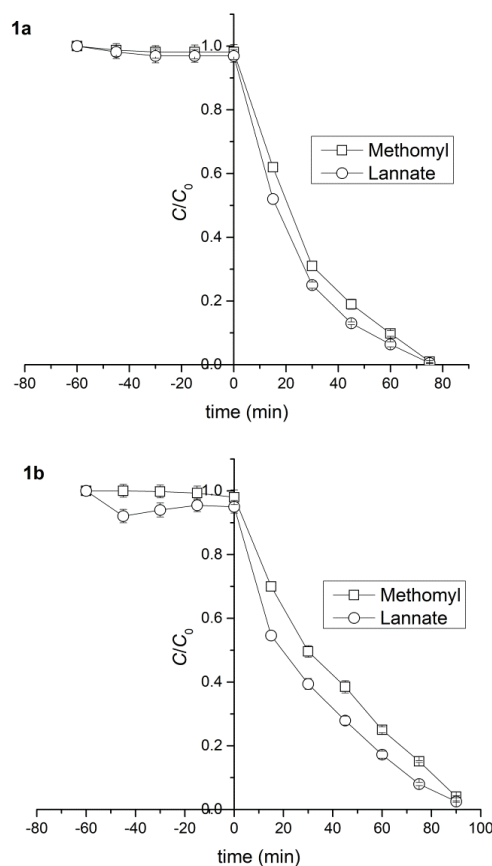


Figure 1. Adsorption and photodegradation of methomyl (pure (pH 5.6) and formulated (pH 5.8)) in the presence of $2 \text{ g L}^{-1} TiO_2$ (1a) and $2 \text{ g L}^{-1} ZnO$ (1b).

photolysis at 315–400 nm [2,5,33]. With TiO₂ only a negligible change in concentration was observed: less than 2% of the initial pesticide concentration of pure methomyl, and about 3% of the initial pesticide concentration of Lannate-90 (Figure 1a). In the presence of ZnO, about 1.9% of methomyl was adsorbed, while the adsorption of Lannate-90 on ZnO was about 7.9% (Figure 1b). The obtained results (degradation was observed in the presence of ZnO or TiO₂ under irradiation) confirmed that the processes took place under the photocatalytic regime.

Water solutions of both the insecticide methomyl and its commercial product Lannate-90 showed the absorption peak at 234 nm, and the obtained UV results are in agreement with HPLC results (Figure 1): the decrease in absorption peak during irradiation indicates a degradation of the methomyl molecule both in the solution of pure methomyl and its commercial product Lannate. The degradation of pure methomyl was slower than the degradation of the commercial product Lannate-90 (Figure 1) both with the TiO₂ and ZnO catalysts. In the presence of TiO₂ over the first 15 min of irradiation, the concentration of pure methomyl decreased from 16.2 to 11.1 mg L⁻¹, while the Lannate methomyl concentration decreased from 16.2 to 8.9 mg L⁻¹ (degradation of pure methomyl reached about 32% of the initial pesticide concentration, while degradation of the formulated product was about 45%). After 45 min only 1.05 mg L⁻¹ of pure methomyl and 0.80 mg L⁻¹ of methomyl from Lannate were detected (93.5% of pure methomyl and 95% of methomyl from Lannate were degraded). After 75 min of illumination, methomyl was practically no longer detected in either reaction solution, *i.e.*, pure methomyl and Lannate-90.

The photocatalytic degradation rate of organic contaminants can be well described using the pseudo-first kinetic order [34]:

$$\ln (C_0/C) = kt \quad (2)$$

$$C = C_0 e^{-kt} \quad (3)$$

where k represents the pseudo-first-order rate constant. The constant value was obtained as a slope from the plot $\ln (C_0/C)$ vs. time. The half-time of the pseudo-first order reaction can be calculated according to:

$$t_{1/2} = \ln 2/k \quad (4)$$

The pseudo-first order rate constant for TiO₂ catalyst ($C_0 = 16.2$ mg L⁻¹, $k = 0.0382$ min⁻¹ for pure methomyl and $k = 0.0457$ min⁻¹ for Lannate-90) was calculated (Table 1). When ZnO was used as the catalyst, and considering the first 15 min, a decrease

from 16.2 to 13.7 and from 16.2 to 12.6 mg L⁻¹ for pure methomyl and Lannate-90 was detected, respectively. After 30 min, 11.1 mg L⁻¹ of pure methomyl and 9.7 mg L⁻¹ of methomyl from Lannate were detected. After 60 min of illumination, 58.5% of pure methomyl and 70.2% of methomyl from Lannate were degraded, while concentration of pure methomyl was about 2 mg L⁻¹ and concentration of methomyl from Lannate was about 1 mg L⁻¹ after 90 min of illumination. Also, the pseudo-first order rate constant for the ZnO catalyst was calculated ($C_0 = 16.2$ mg L⁻¹, $k = 0.0147$ min⁻¹ for pure methomyl and $k = 0.0182$ min⁻¹ for Lannate-90, Table 2). The results show that differences in the photodegradation rates in both reactions were significant within the first 30–45 min, indicating an influence of inert ingredients presents in the commercial product Lannate. Also, TiO₂ is better as a catalyst than ZnO for both methomyl and Lannate-90.

Table 1. Pseudo first-order rate constant values of methomyl and Lannate-90 in the presence of TiO₂, corresponding half-life and correlation coefficient

Form	k (min ⁻¹)	$t_{1/2}$ (min)	R^2
Pure (pH 5.6)	0.0382	18.14	0.9960
Formulated (pH 5.8)	0.0457	15.16	0.9997
Pure (pH 2.0)	0.0564	12.29	0.9890
Pure (pH 3.0)	0.0455	15.23	0.9854
Pure (pH 9.4)	0.0167	41.50	0.9784
Pure (pH 10.3)	0.0141	49.15	0.9886
Formulated (pH 2.0)	0.1017	6.81	0.9904
Formulated (pH 3.0)	0.0636	10.90	0.9888
Formulated (pH 9.4)	0.0362	19.14	0.9763
Formulated (pH 10.3)	0.0294	23.57	0.9898

Table 2. Pseudo first-order rate constant values of methomyl and Lannate-90 in the presence of ZnO, corresponding half-life and correlation coefficient

Form	k (min ⁻¹)	$t_{1/2}$ (min)	R^2
Pure (pH 5.6)	0.0147	47.14	0.9918
Formulated (pH 5.8)	0.0182	38.08	0.9904
Pure (pH 2.0)	0.0141	49.15	0.9939
Pure (pH 3.0)	0.0173	40.06	0.9945
Pure (pH 9.4)	0.0168	41.25	0.9884
Pure (pH 10.3)	0.0138	50.22	0.9985
Formulated (pH 2.0)	0.0127	54.57	0.9855
Formulated (pH 3.0)	0.0189	36.67	0.9976
Formulated (pH 9.4)	0.0164	42.26	0.9820
Formulated (pH 10.3)	0.0131	52.90	0.9947

The effect of initial pH

Photodegradation of pesticides in aqueous solution is known to be affected by pH, and the gener-

ation of hydroxyl radicals depends on pH; also, the catalyst surface properties and behavior of a pollutant and its transformation products depend on pH [1,2,5,23,35-39]. The pH value at which the surface of a semiconductor oxide is uncharged is the point of zero charge (pH_{PZC}). Depending on the ionic form of the pollutant, either electrostatic attraction or repulsion would take place and the photodegradation rate would be, as a result, either enhanced or retarded [36].

Methomyl photodegradation was studied at five different pH values: 2.0, 3.0, 5.6 (or 5.8, for Lannate), 9.4 and 10.3 at the methomyl concentration of 16.2 mg L^{-1} . The pH values of 5.6 and 5.8 were obtained by dissolution of pure methomyl and formulated Lannate in deionized water, respectively. The pH 2.0, 3.0, 9.4, and 10.3 of the initial methomyl (and Lannate-90) solutions were adjusted before irradiation by using 0.1 M HCl or NaOH. The results are shown in Figure 2 and Tables 1 and 2.

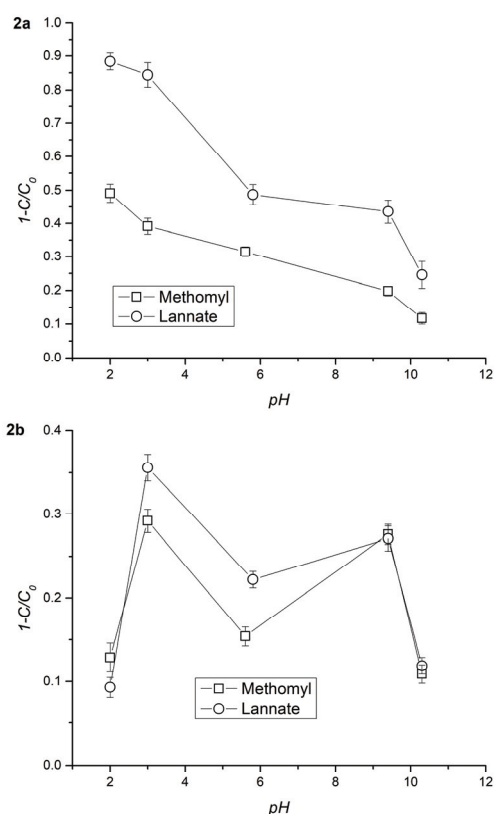


Figure 2. The degradation effectiveness of methomyl and Lannate-90 at different initial pH: in the presence of TiO_2 (2a) and in the presence of ZnO (2b).

In the presence of TiO_2 catalyst, the initial photodegradation rates of pure methomyl and Lannate-90 were found to decrease as the pH of reaction solution increased (Table 1). The contaminant removal value or effectiveness ($1-C/C_0$), presented in Figure 2a, also

decreased with the increase in solution pH. The experimental results are consistent with our previous published results [2,5]. On the other hand, Tamimi *et al.* [19] reported that the rate of methomyl photodegradation in their experiment was the lowest in acidic solution, *i.e.*, it reached a maximum at the neutral pH, and again decreased in the alkaline media. At media pH 5.6-5.8, the degradation rate of pure methomyl was 1.2 times lower ($t_{1/2} = 18.14 \text{ min}$) than the degradation rate of methomyl from Lannate ($t_{1/2} = 15.16 \text{ min}$). The point of zero charge (pH_{PZC}) of TiO_2 is around 6.0 [39] or 6.3 [40], depending on the synthesis procedure. At these pH values, TiO_2 surface is not charged and the inert ingredients have small influence on the reaction rate. In acidic media, TiO_2 is positively charged, so the difference at pH 2.0 and 3.0 between the reaction rates of pure methomyl and Lannate-90 is more pronounced. At pH 2.0, the reaction rate of pure methomyl was 1.8 times lower than the reaction rate of methomyl in Lannate-90. However, this difference is greater in alkaline media (where TiO_2 is negatively charged). At pH 10.3, the reaction rate of pure methomyl is 2.1 times lower than the reaction rate of methomyl in Lannate. It implies that the inert ingredients in Lannate-90 have a catalytic effect on the TiO_2 photodegradation reaction.

It was very hard to generalize the influence of pH on the photocatalytic activity of the ZnO catalyst. The behavior of methomyl and Lannate-90 in the presence of ZnO catalyst (Figure 2b and Table 2) was totally different in comparison with their behavior in the presence of TiO_2 . Low degradation of methomyl, and specially Lannate, in very acidic media (pH 2.0) may be due to the photocorrosion of ZnO at lower pH and decreasing active surface sites [41]. Also, the maximum effectiveness of degradation occurred at pH 3.0. It had been found earlier that photodegradation with ZnO was more effective in acidic than in alkaline media [23] due to a greater electrostatic attraction between methomyl molecules and ZnO surface. Also, the degradation of Lannate was more pronounced than the degradation of pure methomyl in acidic media. The point of zero charge (pH_{PZC}) of ZnO is (9.0 ± 0.3) according to literature [38], and ZnO surface is mostly negative charged above that value. At pH 9.4, which is much closer to the point of zero charge, the degradation rates of pure methomyl and Lannate were similar. At pH 10.3, the degradation rate of methomyl (and Lannate) showed a decreasing trend. It means that inert ingredients from Lannate have no influence on the reaction rate in alkaline media. The ZnO surface should be positively charged in acidic media. Therefore, as the influence of inert

ingredients on the reaction rate is higher in acidic than in alkaline media, it is very likely that the ingredients are negatively charged and that attraction occurs between the ingredients and ZnO surface. As the medium pH increased those interactions became higher: under media pH 5.6–5.8 the degradation rate of the formulated methomyl was 1.25 times higher ($k = 0.0182 \text{ min}^{-1}$) than the degradation rate of pure methomyl ($k = 0.0147 \text{ min}^{-1}$). Finally, at the end, these interactions in alkaline media are smallest. The ZnO surface and the ingredients are both probably negatively charged.

Optical characterization

The optical properties such as the band gap of TiO₂ and ZnO catalysts used in this work were also studied. The optical band gap determination is available as Supplementary Material. The determined value for the band gap of TiO₂ (3.3 eV) is higher than the reported one (3.2 eV) [42]. On the other hand, the determined value for the band gap of ZnO (3.2 eV) is lower than some reported values (3.37 eV [43]), although similar values can be found in the literature [44]. The band gap of the semiconductor should strongly influence the activity of photocatalyst. If only literature values of TiO₂ and ZnO are considered it is obvious why TiO₂ is the better catalyst. It is obvious that the degradation effectiveness of TiO₂ and ZnO catalysts used in this work is not solely correlated to their optical band gaps (if determined band gaps are taken in consideration) but also to the oxidation “power” of electrons, surface properties, charge transport, etc. [45].

Morphological characterization (ATR-IR analysis)

In order to evaluate changes in the catalyst structure during photocatalyzed degradation of methomyl and Lannate, IR analysis of TiO₂ and ZnO catalysts before and after degradation reaction was performed (Supplementary Material). The TiO₂ Degussa spectrum is characterized by the strong vibration below 1000 cm⁻¹. This can be assigned to the Ti-O bond surface vibration [46]. The bands in frequency range 1400–1460 cm⁻¹ can be assigned to the Ti-O-Ti vibration [47]. The absorption in the range 1620–1640 cm⁻¹ corresponds to the bending vibration of the O-H bond (chemisorbed water). The broad peak in the range 3000–3500 cm⁻¹ is due to the surface adsorbed water [48]. The peaks at around 2927 and 2855 cm⁻¹ corresponds to the stretching of the C-H bond (symmetric and asymmetric). These peaks probably originate from organic residues remained after calcination of TiO₂ [49]. The spectra of TiO₂ after photocatalytic degradation of methomyl and Lannate are charac-

terized by several additional peaks, at 1690, 1217 and 1155 cm⁻¹, which correspond to C=O and C-O groups of degradation products.

ATR-IR spectra of ZnO Merck before degradation as well as after 75 min of photocatalytic degradation of methomyl and Lannate are available as Supplementary Material. The ZnO spectrum shows strong vibration below 1000 cm⁻¹ which corresponds to Zn-O stretching and deformation vibration [50,51]. The peaks in the region 2800–3000 cm⁻¹ correspond to the stretching of the C-H bond probably as a result of the presence of organic residues that remained after calcination. The peak at 1560 cm⁻¹ shows O-C-O stretching vibration of adsorbed carbonate anion. The peaks around 1400 cm⁻¹ indicates CH₃ bending as a result of present Zn(CH₃COO)₂·2H₂O [52]. The spectra of ZnO after photocatalytic degradation of methomyl and Lannate are characterized by several additional peaks, at 1221, 1159 and 1064 cm⁻¹. These new peaks originate from degradation products and can be assigned to C-O vibrations. In addition, increase in peak intensity can be observed in the region 2800–3000 cm⁻¹.

The effect of formulation (inert ingredients)

Inert ingredients may have different degrees of influence on the photodegradation reaction of active ingredients, either increasing or retarding its rate [23]. The differences in photodegradation rates between pure methomyl and the commercial product Lannate-90 could be attributed to the fact that methomyl, which has good solubility in water (57.9 g L⁻¹, 25 °C), is formulated as a soluble powder (SP). A soluble powder consists of the active ingredient mixed with water soluble inert ingredients, such as wetting agents (surfactants, anionic or nonionic), filler (used as diluents, some kind of inorganic salt, lactose, etc.), probably some dye, to ensure optimum results in product dissolution and application [13,26]. Wetting agents are used to facilitate rapid dissolution of the product in water by lowering the interfacial tension between liquid and solid and spreading on plant foliage [13,53]. After dissolution the formulation acts as a true solution. The presence of a wetting agent improves the solubility and spreading of methomyl. Also, the wetting agent makes methomyl more available for oxidation. As a result, the photodegradation rate is a little bit higher than in the case of pure methomyl. On the other hand, the anionic surfactant sodium dodecyl sulphate promotes adsorption of rhodamine B on the TiO₂ surface and expands the absorption of light from the UV to the visible region [54]. This may be the reason of better efficiency of TiO₂ in comparison to

ZnO in photodegradation of methomyl. Also, different sugars (glucose, lactose, etc.), which might be present in the formulation, may increase the surface area of catalysts and increase catalyst efficiency [55].

Mineralization study of pure methomyl and Lannate-90

Complete mineralization of contaminants is the target of any photocatalytic process including methomyl, and photocatalytic degradation of pure methomyl had been the subject of several earlier papers [1,2,4,5,18-21]. As a result of methomyl mineralization through different photochemical processes, sulfate, nitrate, and ammonium ions have been released and detected in different concentrations in reaction solutions. There are no literature data on ZnO and TiO₂ photocatalytic degradation of methomyl commercial products. In these experiments, sulfate, nitrate and ammonium ions were confirmed in the case of pure

methomyl, while only sulfate and nitrate ions were detected in the case of the commercial Lannate-90 (Figure 3). Ion chromatography data show that mineralization of sulfur and nitrogen from the methomyl molecule was incomplete in all cases (maximum detected values were 6.9, 1.5, and 1.3 mg L⁻¹ for sulfate, nitrate, and ammonium ions, respectively). Complete mineralization of organic carbon from methomyl molecules (pure and commercial) was not achieved during both photocatalytic reactions (TOC elimination varied from 60 to 80% (Figure 3)). These results also suggest the formation of new organic compounds in the photocatalytic system. The HPLC-MS analysis confirmed the formation of three methomyl photodegradation products during TiO₂ photodegradation of pure and formulated methomyl.

Identification of photodegradation products during TiO₂ degradation, HPLC/MS analysis

An HPLC-MS analysis was performed only for TiO₂ catalyzed reactions since TiO₂ was found to be a better catalyst. In both degradations (pure methomyl and its commercial product Lannate-90), the same transformation products were identified. The results are presented in Table 3 and Figure 4. Three major transformation products of photocatalytic degradation were identified: (*E*)-methyl-*N*-hydroxyethanimidothioate (methomyl oxime), transformation product I (ion detected at *m/z* 178; (*E*)-methyl-*N*-hydroxymethylcarbamoyloxyethanimidothioate) and transformation product II (ion detected at *m/z* 148; (*E*)-methyl-*N*-carbamoyloxyethanimidothioate).

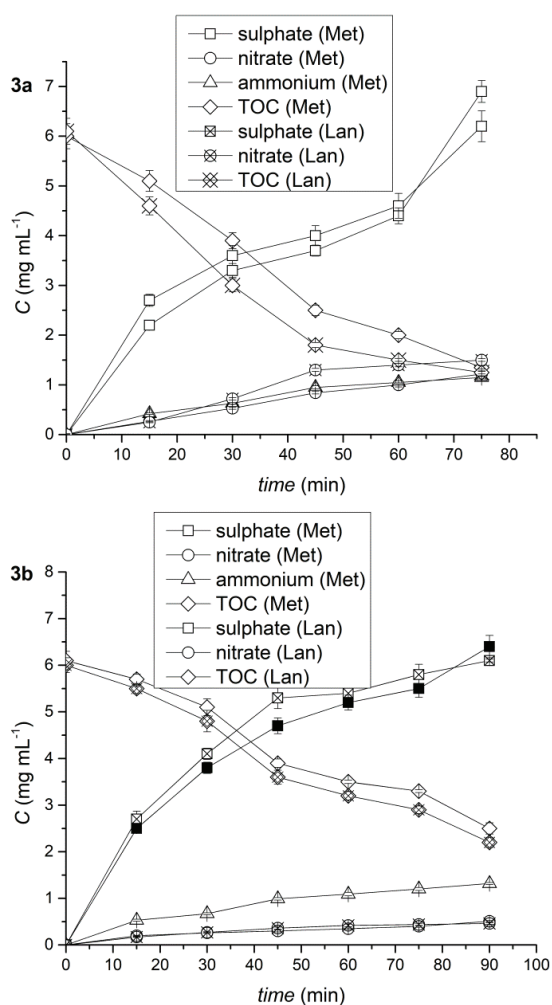


Figure 3. Degradation and mineralization of methomyl and Lannate-90 in the presence of 2 g L⁻¹ TiO₂ (3a) and 2 g L⁻¹ ZnO (3b).

Table 3. MS and MS² data of selected precursor ion detected in photodegradation samples of methomyl and Lannate-90 in the presence of 2 g L⁻¹ of TiO₂

Compound	Mw	MS, <i>m/z</i>	MS ² (relative abundances), <i>m/z</i>
Methomyl	162	163 [M+H] ⁺ 185 [M+Na] ⁺ 325 [2M+H] ⁺	122 (100), 88 (55), 130 (10), 163 (7), 106 (6)
Methomyl-oxime	105	106 [M+H] ⁺	88 (100), 106 (25)
Transformation product I	178	179 [M+H] ⁺ 201 [M+Na] ⁺	/
Transformation product II	148	149 [M+H] ⁺	88 (100), 108 (25)

Similar degradation rates were achieved for pure methomyl and Lannate-90 preparation (Supplementary material). Almost complete photodegradation of methomyl in both analyzed systems was found to occur after 45 min of illumination time. During methomyl degradation, increase was detected in the con-

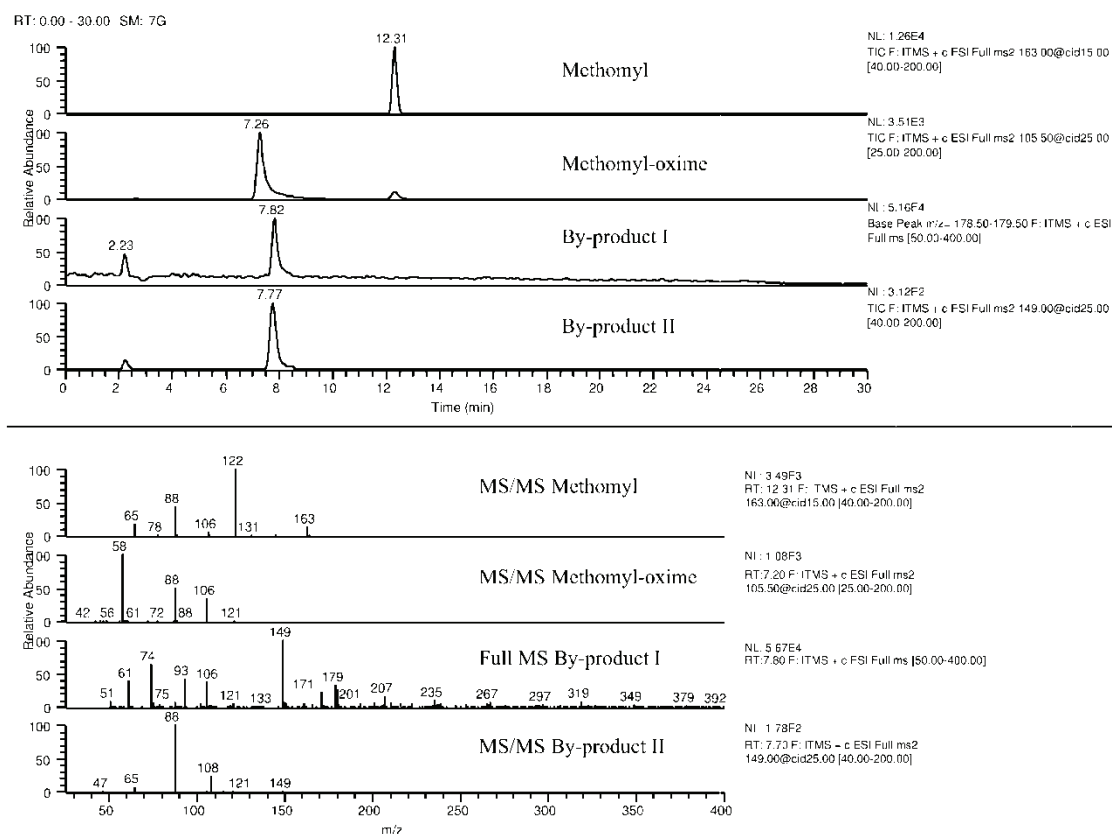


Figure 4. HPLC/MS/MS data for methomyl and Lannate-90.

centrations of three products: methomyl oxime (ion at m/z 106), transformation product I (ion at m/z 179) and transformation product II (ion at m/z 149). The highest intensities of the peaks corresponding to these products were found in the period from 10 to 40 min. A similar profile of time-dependent concentration change of all three transformation products was found in pure methomyl and Lannate-90 preparation (Supplementary material). The formation of methomyl oxime (Supplementary material) is more intensive during the photodegradation process that takes place in the reaction mixture with pure methomyl. On the other hand, similar behavior was found for transformation product I both for pure methomyl and Lannate-90 preparation, with somewhat higher values observed for Lannate-90 (Supplementary material). Conversely, transformation product II had higher intensity in pure methomyl samples (Supplementary material).

The identified intermediate transformation products include methomyl oxime (ion at m/z 106), transformation product I (ion at m/z 179) and transformation product II (ion at m/z 149). Tamimi *et al.* [20] have also identified intermediate degradation products, such as methomyl oxime, oxalic and glycolic acid. In our previous work [1] we had also detected methomyl oxime as the main intermediate. The deg-

radation transformation products obtained in the present study are similar to the intermediates generally reported in other literature sources. This is mainly due to similar photodegradation mechanisms achieved by the attack of the generated active species, *i.e.*, hydroxyl radical, on the studied substrate. By summarizing literature data and the results presented here, and by identifying intermediate transformation products, a possible degradation pathway is presented in Figure 5.

Oxidative environment in the analyzed irradiated mixture induced several molecular transformations:

- elimination of methylisocyanate (rupture of O=C-O bond) produced methomyl oxime (M_w 105);
- initial hydroxylation of the methyl group attached to the nitrogen atom produced methomyl methylol, transformation product I (M_w 178);
- demethylation of methomyl produced (*E*)-methyl-*N*-carbamoyloxyethanimidothioate with molecular mass of 148 (Figure 5).

The detected degradation products were subjected to a subsequent MS² analysis. Transformation product I showed no detectable fragments in MS² spectra. On the other hand, methomyl showed three fragmentation paths: first - by losing fragment M_w 33, an ion at m/z 130 was produced; second - two-

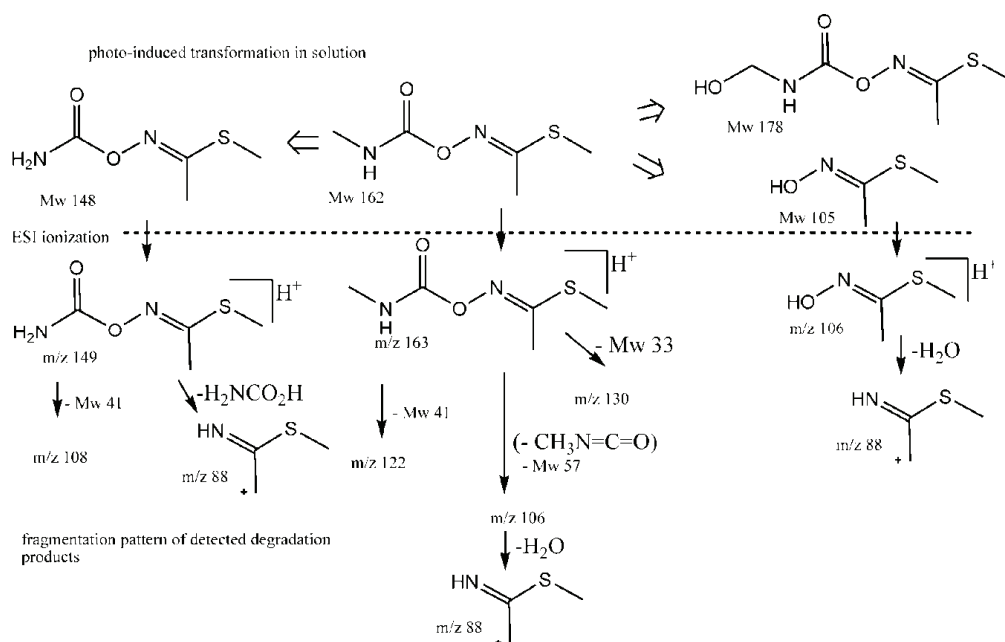


Figure 5. Photo-induced transformation of pure methomyl and Lannate-90 in solution and main fragmentation pathways of methomyl oxime, transformation products I and II.

-step defragmentation by losing methyl isocyanate (*Mw* 57) produced a *m/z* 106 ion, and in the second step dehydration of the formed ion produced 2-imino-2-(methylthio)ethan-1-ylum ion (ion at *m/z* 88); third -removal of the fragment with *Mw* 41 produced an ion at *m/z* 122. The third detected photoproduct, transformation product II, showed two fragmentation paths: loss of fragment *Mw* 41 gave an ion at *m/z* 108 and the elimination of carbamic acid produced an ion at *m/z* 88.

CONCLUSION

The paper proves the effectiveness of heterogeneous photocatalysis for the removal of the pesticide methomyl and its commercial products Lannate-90 from water. Two catalysts were employed and it was found that TiO_2 is better catalyst than ZnO for both methomyl and Lannate-90. Pure methomyl disappeared at a slower rate than Lannate-90 and the degradation of both, commercial and pure methomyl was affected by initial pH. Also, the mineralization of sulfur, nitrogen and organic carbon from methomyl molecules was always incomplete. During the TiO_2 photodegradation of pure methomyl and Lannate-90 three major transformation products were identified and confirmed by LC/MSⁿ analysis. Finally, the main fragmentation pathway of photodegradation was proposed based on photoproducts. The obtained results highlight the fact that inert ingredients from commercial products can influence the photodegradation

rate of the active ingredient in different ways. This could be very important for the pesticide industry since the appropriate selection of formulation type (choice of inert ingredients) can increase the removal rate of pesticide residues from contaminated water.

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NAUČNI RAD

STUDIJA FOTOKATALITIČKE DEGRADACIJE METOMILA I NJEGOVOG KOMERCIJALNOG PROIZVODA LANNATE-90

Ispitivana je fotokatalitička degradacija karbamatnog insekticida metomila i njegovog komercijalnog proizvoda Lannate-90 u vodenoj suspenziji TiO₂ i ZnO koristeći Osram ultra-vitalux lampu (315-400 nm). Cilj ispitivanja je bio proučavanje i poređenje stepena fotohemijske degradacije čiste aktivne komponente i njenog formulisanog preparata da bi se pokazao uticaj inertnih sastojaka iz formulacije na degradacioni proces. Utvrđeno je da je fotohemijska degradacija aktivne supstance metomila sporija od degradacije njegovog komercijalnog proizvoda Lannate-90. Fotodegradacija metomila i Lannate-90 je ispitivana pomoću UV-VIS spektrofotometrije i tečne hromatografije, a njihova mineralizacija je praćena korišćenjem jonske hromatografije i TOC analize. Sposobnost apsorpcije svetlosti katalizatora je određena pomoću difuzno-refleksione spektroskopije, dok je njihova stabilnost proučavana pomoću IR spektroskopije. Zahvaljujući rezultatima HPLC-MS/MS analize identifikovani su njihovi degradacioni proizvodi i predloženi su verovatni fotodegradacioni putevi.

Ključne reči: Lannate-90, metomil, fotokataliza, titan-dioksid, cink-oksidi.