

PHOTOCHEMICAL PROCESSES FOR REMOVAL OF CARBAMATE PESTICIDES FROM WATER*

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A large number of pesticide active ingredients have been registered and marketed for pest control purposes around the world. Most pesticides, including carbamates are resistant to chemical and natural photochemical degradation, so that developing adequate methods for remediation of contaminated waters is a priority. There are different methods for removing carbamate pesticide residues from water, and photodegradation methods are discussed in this study. According to literature data, the most beneficial photochemical processes for removal of pesticides from water are two well-known Advanced Oxidation Processes: heterogeneous photocatalysis with semiconductor oxides TiO₂ and ZnO, and homogeneous photo-Fenton treatment, as well as direct UV photolysis. Photochemical investigations may contribute toward our better understanding of carbamate pesticide behavior in the environment, i.e. more information on the degradation time of active ingredients, their activity and environmental fate can be obtained by studying the kinetics of any photochemical reaction.

Keywords: methomyl, carbofuran, photodegradation, photolysis, photocatalysis

Introduction

Water is an essential compound for life on Earth and its quality is crucial for the future of humanity. The demand for clean water is expected to increase by midcentury, according to [1]. Only a small fraction of the available surface water has the quality necessary for human and industrial use, and improvement of technologies for treatment of wastewater, remediation of polluted water and elimination of micropollutants from water are very important expectations. Removing pesticide residues from water is very difficult and pesticide pollution in surface and groundwater has been recognized many years ago as an important issue in a number of countries. There are two sources of pesticides that contaminate aqueous media: (1) wastewaters from pesticide manufacturing plants, agricultural fields, and equipment rinsing operations and (2) surface water and groundwater. Whereas wastewaters often contain very high level of pesticides (a milligram per liter or more), surface water and groundwater usually contain only trace amounts of pesticides (a microgram per liter or less), but these often occur as a more complex mixture [2].

Carbamates are a large group of pesticides which have been extensively used over the past seventy years primarily as insecticides, but also as herbicides and fungicides. This group includes more than 50 different chemicals which are identified as a group of pesticides with a

potential to affect the functioning of the nervous system. Due to their widespread use in agriculture and relatively good solubility in water, carbamates represent potential contaminants of both surface and ground water resources [3].

Methomyl and carbofuran (Figure 1) are carbamate pesticides which have been in use for many years. The Environmental Protection Agency, World Health Organization, and European Commission have classified methomyl and carbofuran as highly toxic compounds. Methomyl (IUPAC name: S-methyl N-(methylcarbamoyloxy)thioacetimidate, CAS No.:16752-77-5) is a systemic insecticide and acaricide with contact and abdominal actions. It was first introduced in 1966 by Du Pont Company. Methomyl is used for foliar treatment of vegetables, fruit field crops, cotton, etc. According to [3], methomyl is a hazardous compound, and it is a pollutant of environmental concern because of its high solubility in water (57.9 g/L at 25 °C). Additionally, since its sorption affinity to soils is rather low, various amounts of methomyl have been detected in ground and surface waters across Europe and America [4]. The formulation types used for this active ingredient are SL, SP, and WP. Carbofuran (IUPAC name: 2,3-dihydro-2,2-dimethylbenzofuran-7-ylmethylcarbamate, CAS No.:1563-66-2) is a systemic insecticide, acaricide, and nematocide with predominant contact and

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abdominal actions. It was introduced in 1965 under the trade name Furadan by FMC Corporation. Carbofuran has relatively good solubility in water (0.35 g/L at 25 °C) and a resulting great potential for groundwater and surface water contamination [3,5]. Moreover, it can produce extensive negative effects in aqueous ecosystems [3,6]. This active ingredient is prepared as FS, GR, SC or WP formulation.

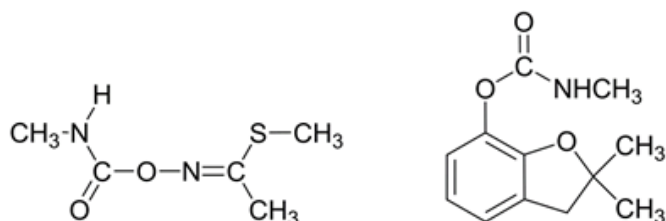


Figure 1. Structure of methomyl (left) and carbofuran (right).

Various processes have been investigated in order to reduce pesticide concentrations in water and to minimize the potential health risks. Conventional wastewater treatments involve mechanical, biological, physical and chemical processes. These methods of water disinfection and decontamination can be a successful solution to a lot of problems caused by pesticide concentrations. However, these methods are often exacting in large systems, in terms of required chemicals, energy and labour, and thus require considerable infusion of capital, engineering expertise and infrastructure, all of which precludes their widespread use around the world. Furthermore, intensive chemical treatments, involving ammonia, chlorine compounds, hydrochloric acid, sodium hydroxide, ozone, permanganate, aluminum and ferric salts, coagulation and filtration aids, anti-scalants, corrosion control chemicals, and ion exchange resins can add to the problems of contamination and salting of freshwater sources. Physical treatments involving coagulation, flocculation, sedimentation, flotation, filtration, adsorption, etc., transfer the pollutants from the liquid phase to a new phase rather than eliminate them. Chemical treatments can also release other hazardous materials into the air or into "purified" water and thus replace the original contamination by different pollutants [7].

Photochemistry is the chemistry of reactions induced by light, and photodegradation occurs as a degradation of photodegradable molecules caused by the absorption of photons, particularly those wavelengths found in sunlight, such as UV, VIS or IR light. Photodegradation includes photodissociation, i.e., the breakup of molecules into smaller pieces by photons. It also includes the change of molecule shape to make it irreversibly altered, such as the denaturation of proteins, as well as the inclusion of different atoms or molecules. A common photodegradation reaction is oxidation and it is used by some drinking water and wastewater facilities to destroy pollutants. Photochemical processes could be used for treatment of many hazardous organic contaminants in water, aqueous waste streams, soils and groundwater, and for decontamination

of pathogen water [8].

The aim of this paper is to present several technologies based on photochemical processes for the degradation of the carbamate pesticides, methomyl and carbofuran from water and wastewaters under near-ambient conditions. The most beneficial processes for removal of pesticide residues from water are direct UV photolysis and Advanced Oxidation Processes (AOPs). This presentation focuses on the photolytic and photocatalytic removal of methomyl and carbofuran at low concentration from different types of water, upon the activity of UV, visible or natural solar light, in the presence of TiO₂ and ZnO catalysts, and using Fe-ZSM-5-zeolite and AlFe-pillared montmorillonite. The effects of different operational parameters, such as the initial concentration of pesticides and catalysts, pH, and initial salt concentration were examined. A comparative study on the degradation of carbofuran and its commercial product, Furadan 35-ST, at 315-400 nm in ZnO aqueous suspension will also be presented to evaluate the effects of the inert ingredients, present in the commercial product, on carbofuran photodegradation. The rate of pesticides photodecomposition was measured using UV spectroscopy and high-performance liquid chromatography (HPLC), while their mineralization was investigated by ion chromatography (IC) and total organic carbon analysis (TOC). Photodegradation products of pesticides were identified based on the results of high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) and gas chromatography-mass spectrometry (GC-MS), and their photodegradation pathways are proposed.

Photolysis

Photolysis is a direct photodegradation reaction or photodegradation process that involves no catalyst and uses light only for degradation of various molecules such as different environmental contaminants, including pesticide residues. Direct irradiation can promote pesticides into their excited singlet states, which may then cross into the intersystem and produce long-lived triplet states. Such excited states can then undergo homolysis, heterolysis or photoionization processes [9,10]. Photolysis takes place in various aqueous and non-aqueous media, such as water (river, deionized, distilled, seawater, tap water, with different ions, with O₂ and O₂/O₃, etc.), different aqueous solutions and media (buffers solutions, water with ions, methanol/water, chloroform/water, ethanol/water), different organic solvents (*i*-propanol, *n*-hexane, methanol, 2-propanol, benzene, acetonitrile, mixtures of the solvents, etc.), and other media (water/soil suspension, thin films, glass, etc.) [9]. Since direct photodegradation by solar light is limited, various lamps were used for irradiation of contaminated water or non-water solutions: low-, medium-, and high-pressure mercury vapor lamps, xenon, fluorescent, mercury-xenon lamps, etc. The kinetics of photolysis reactions in aqueous solution depends on various reaction parameters such as type of light, lamp distance, temperature, initial concentration of pesticides, type of water, pH, the presence of humic and fulvic acids,

the presence of O_2 , O_3 , O_2/O_3 and H_2O_2 , the presence of inorganic ions and organic matter dissolved in water, etc. [9,11-13].

The photolysis of 16.22 mg/L (1×10^{-4} M) of methomyl in different types of water (deionized, distilled, and sea water) using an Osram mercury lamp (2×8 W) was studied, and the influence of reaction parameters to pesticide degradation was investigated [11,13,14]. All experiments were performed under monochromatic 254 nm ultraviolet light since 366 and 315-400 nm light had no effect on methomyl photolysis, as previously established [13]. The photolytic studies showed that methomyl was effectively decomposed by 254 nm light in the three types of water (including seawater), and the photolysis rate depended on the lamp distance, water type, reaction temperature, and pH. The reaction rate of methomyl removal decreased with the increase of lamp distance and the reaction rate was 3.7 times higher ($k = 0.0194 \text{ min}^{-1}$) when the lamp was placed at 20 mm from the reaction mixture surface, in comparison to the reaction ($k = 0.0053 \text{ min}^{-1}$) when the lamp was placed at 200 mm. Also, the influence of water type on degradation process was assessed in deionized (pH 5.2), distilled (pH 5.5), and seawater (pH 7.9). The results are shown in Table 1: all reactions followed first-order kinetics and the reaction rate was highest in distilled water and lowest in seawater. The obtained results suggest that certain ions in distilled water promote photolysis of methomyl, while some ions from seawater (such as Cl^- , HCO_3^- , SO_4^{2-} , etc.) decelerated the photolytic process. In addition, it was found that the reaction rate increased in a temperature range from 10 °C ($k = 0.0076 \text{ min}^{-1}$) to 50 °C ($k = 0.0098 \text{ min}^{-1}$), while half-lives decrease from 91.20 to 70.73 min, respectively. It was also found that reaction rate was highest in neutral (pH 6.00) and lowest in acidic media (pH 3.15) (Figure 2).

Table 1. Kinetics of methomyl photolysis under 254 nm [11,13]

Water type	Parameters		
	k (min^{-1})	R	$t_{1/2}$ (min)
Deionized	0.007	0.999	97.63
Distilled	0.009	0.999	79.67
Sea	0.006	0.994	123.78

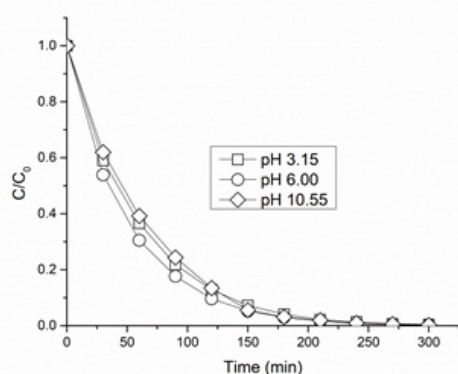


Figure 2. The effect of pH on the photolysis rate of methomyl (distilled water, lamp distance 100 mm, temperature 20 °C).

Advanced Oxidation Processes (AOPs)

According to [15], complete degradation of organic pollutants, including pesticides and related compounds is not possible by conventional physical, chemical and biological treatments, because they only transfer the contaminants from one phase to another. Advanced Oxidation Processes (AOPs) have great capability in water treatment and purification, including pesticides and other deleterious contaminants. AOPs have been precisely defined as "near ambient temperature and pressure water treatment processes which involve the generation of hydroxyl radical in sufficient quantity to effective water purification" [16]. These processes have recently attracted increasing attention, and there are numerous studies relating to the fundamental and applied aspects of AOPs [5,7-32]. AOPs, which utilize hydroxyl radical, include catalytic and photochemical methods and have H_2O_2 , O_3 or O_2 as the oxidant. AOPs include different processes: ozonation, UV-based processes, sonolysis, radiolysis, photocatalysis, Fenton, photo-Fenton and Fenton *like*-reactions, electrochemical oxidation, wet air oxidation, ultrasound and microwave processes, as well as all different combinations of the mentioned processes. The principal active species in these systems is the hydroxyl radical $\cdot OH$, which is a powerful, extremely reactive and non-selective oxidant for most organic contaminants, including aromatic and halogenated compounds, pesticides, halogenated hydrocarbons, etc. [8,17,18,22,23,33,34]. Hydroxyl radical has oxidation potential of $E^0 = 2.73$ V and shows faster rates of oxidation as compared to other conventional oxidant [23,35,36]. Most organic compounds react with $\cdot OH$ by adding or absorbing hydrogen to form a carbon-charged radical. The carbon-charged radical reacts with molecular oxygen to form a peroxy radical that undergoes subsequent reactions producing oxidation products (ketones, aldehydes, and alcohols) [9,17,34,37]. The main advantage of AOPs is the almost complete mineralization of many organic pollutants to water, CO_2 , mineral salts, and non-toxic compounds [7,17,32].

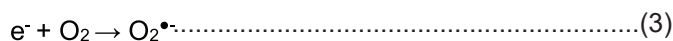
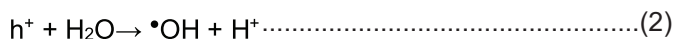
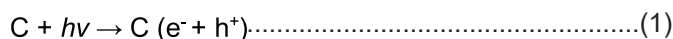
AOPs involve different homogeneous (when both the catalyst and reactant are in the same phase) and heterogeneous (when the reactant and catalyst are in different phases) photocatalytic processes. Homogeneous photocatalytic oxidation employs various oxidation system (Fenton reagent, H_2O_2 , O_3 , etc.) either alone or in combination with UV, visible, and natural solar light [17,38]. Heterogeneous photocatalytic processes, named heterogeneous photocatalysis are a combination of UV or solar light, various catalysts (TiO_2 , ZnO , ZnS , ZrO_2 , CdS , SnO_2 , WO_3 , etc.) and different oxidants (H_2O_2 , $K_2S_2O_8$, KIO_4 , $KBrO_3$, etc.) [11,21,24,26].

The chemistry of AOPs is very complex due to a variety of reactions involved, and many details on improving the efficiency of photo processes are still unknown. The fundamentals of AOPs include the generation and type of radicals, the fate and type of reactions, the fate of compounds during reactions, etc. Radical reactions in-

clude three stages: the initial stage of radical generation, the radical reaction stage, and termination stage of radical recombination. There are several different options for radical generation since not only •OH radicals are generated, but also other radicals may have considerable contributions as parts of chain reactions depending on the conditions of applications and processes [9,17]. Consequently, it is not possible to give a comprehensive description of all AOPs, but several currently employed processes have been described.

Heterogeneous photocatalysis

Photocatalysis is a combination of photochemistry and catalysis, a process where light and catalysis are simultaneously used to promote or accelerate a chemical reaction. Direct light absorption is one of the significant advantages of photocatalysis over thermally active catalytic processes. In comparison with classical treatments photocatalysis currently appears to be an excellent method of final treatments of samples containing organic pollutants [39-41]. The main equations of the heterogeneous photocatalysis are [7,17,42,43]:



The semiconductor titanium dioxide has been widely used as a photocatalyst for starting a chain of redox reactions during the process of water purification [7,11,21,26]. It is the most common semiconductor used on photocatalytic processes because of its high catalytic activity, non-toxicity, chemical and biological stability, water insolubility, etc. [44]. Also, it does not involve mass transfer, it can be carried out under ambient conditions (atmospheric oxygen is used as oxidant), has strong resistance to chemical breakdown and photocorrosion and may lead to complete mineralization of organic carbon into CO₂ [7]. TiO₂ occurs in three crystals forms: anatase, rutile, and brookite. Degussa P-25 has effectively become a standard [7,45-47]. To perform a heterogeneous photocatalytic reaction activated by light it is necessary to use semiconductors with the adequate "band-gap". TiO₂ has a high band-gap, of 3.2 eV, being consequently activated only by radiation below 380 (390) nm, i.e., using only 10% of the sunlight spectrum [7]. The mechanism of catalytic action of TiO₂ is well-known [7,11,17,31,42,44]. Among the various semiconductors employed, TiO₂ photocatalytic reaction has received increasing attention because of its low cost when using sunlight as the source of irradiation [7].

The semiconductor zinc oxide is also frequently used as a catalyst in heterogeneous photocatalytic processes and has good characteristics in degradation and mineralization of organic pollutants [11,24,48,49]. ZnO may have one of three types of crystal structure: hexagonal

wurtzite, cubic zinc blende, and cubic rock salt, where wurtzite is the most stable structure [50]. ZnO has a wide band gap (3.2 eV) and due to its low production cost and its electrical and luminescence properties it has been studied as a potential photocatalyst [24,50]. The quantum efficiency of ZnO is significantly larger than that of TiO₂. Thus, the greatest advantage of ZnO in comparison to TiO₂ is that it absorbs over a large fraction of the UV spectrum (i.e. solar spectrum) and according the literature data the corresponding threshold wavelength of ZnO is 440 nm [7], relatively to 425 nm [48], and ZnO is a more suitable photocatalyst for use under visible light conditions [51,52]. In addition, photocatalytic degradation with ZnO is more effective in acidic than in alkaline media [53] because photodecomposition and photo-corrosion of ZnO occurs in alkaline media [53,54]. It has been reported that during photocatalytic degradation of the herbicide clopyralid in water, ZnO Merck was a better catalyst than TiO₂ P-25 (Evonik) [55]. Also, Evgenidou et al. [56] have reported that ZnO appeared to be the more efficient catalyst in comparison to TiO₂, especially at high concentrations (above 0.2 g/L of catalyst). Some of the experimental results have also shown that ZnO exhibits a higher photocatalytic activity than TiO₂, especially when the degradation of industrial effluents occurs at neutral pH [52]. The mechanism of catalytic action of ZnO is also well-known [11,48,53,54].

The rate and efficiency of a heterogeneous photocatalytic reaction depends on a number of factors, such as the initial concentration of reactant, initial concentration of catalyst, pH, light intensity and radiant flux, temperature, concentration of oxygen, the presence of scavengers and various ions, etc. [7,11,13,14,24,57,58].

The photocatalytic removal of 16.22 mg/L (1 x 10⁻⁴ M) of methomyl aqueous solution under UV/VIS (366 and 315-400 nm) and natural solar light was examined in the presence of two well-known semiconductor oxides TiO₂ and ZnO, and the influence of reaction conditions (initial concentration of methomyl, catalysts type and concentration, pH, and presence of Cl⁻ ions) was studied [11,13,14,57,58]. For photocatalytic methomyl degradation at 366 and 315-400 nm all experiments were performed using 1.0-3.0 g/L of either TiO₂ (Merck Eu-solex T, anatase modification) or ZnO (Merck) and the optimal concentration of catalysts was found to be 2.0 g/L under both 366 (Figure 3) and 315-400 nm, and ZnO was always the better catalyst than TiO₂ under the same reaction conditions (Table 2). A pseudo-first-order kinetic model was confirmed on the basis of the Langmuir-Hinshelwood (L-H) mechanism [13,58]. In addition, the effect of the initial methomyl concentration on photodegradation was studied and the results obtained are presented in Table 3. The results given in Table 3 show that an increase in initial methomyl concentration leads to a lower photodegradation rate. The photocatalytic removal of methomyl at 366 nm was studied at three different pH values (3.5, 5.6 and 9.0), adjusted by the addition of HCl (3.5) or NaOH (9.0), where the third pH value was of a

pure insecticide solution in deionized water. The results imply that the removal rate was the highest in acidic solution and the lowest in alkaline solution (Figure 4). For the removal of methomyl at 315-400 nm, four different pH values (2.0, 3.5, 5.6, and 9.0) were examined and the results also imply that the removal rate was the highest in acidic solution and the lowest in alkaline solution [13]. It was also found that for degradation at both 366 and 315-400 nm, the presence of NaCl led to reaction inhibition due to the scavenging properties of chloride ions [11,13,14,58]. The results of the methomyl photocatalytic removal (with 0.1 or 0.2 g/L of TiO₂ and with 0.15 g/L of ZnO) under natural sunlight are presented in Table 4. In all cases methomyl dissipation followed the pseudo-first kinetic order. Table 4 shows that ZnO is the better catalyst for deionized water, while the lower concentration of TiO₂ is better for distilled water. In seawater, methomyl disappeared approximately 2 times faster in the presence of ZnO than in the presence of TiO₂. The ion chromatography results confirmed that methomyl mineralization led to the formation of sulfate, nitrate, and ammonium ions (detected in various relative concentrations) during all investigated processes [11,13,14,58].

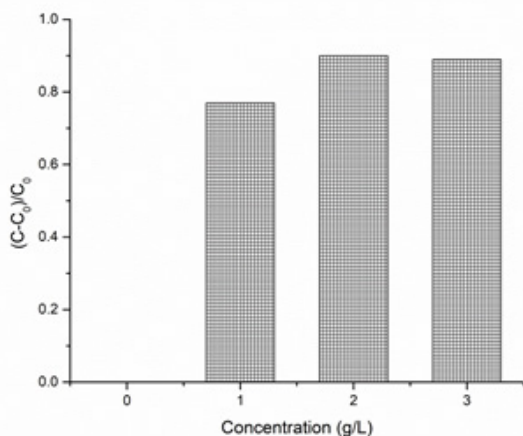


Figure 3. The effect of the TiO₂ concentration on the photodegradation efficiency of methomyl at 6 h irradiation time (methomyl concentration 16.22 mg/L).

Table 2. Kinetics of methomyl photodegradation under 315-400 nm [11,13,58]

Methomyl	With 2.0 g/L of TiO ₂			With 2.0 g/L of ZnO		
	<i>k</i> (min ⁻¹)	<i>R</i>	<i>t</i> _{1/2} (min)	<i>k</i> (min ⁻¹)	<i>R</i>	<i>t</i> _{1/2} (min)
Deionized water	0.0047	0.9941	147.48	0.0100	0.9988	69.31

Table 3. Kinetics of methomyl degradation under 315-400 nm in the presence of 2.0 g/L of TiO₂ [11,13,58]

Co (mg/L)	16.22	12.15	8.10	4.05
<i>k</i> (min ⁻¹)	0.0047	0.0051	0.0070	0.0077
1/ <i>k</i> (min)	212.77	196.08	142.86	129.87
<i>R</i>	0.9998	0.9851	0.9771	0.9620

Table 4. Kinetics of methomyl photodegradation under natural solar light [11,13]

Methomyl	With 0.1 g/L of TiO ₂			With 0.2 g/L of TiO ₂			With 0.15 g/L of ZnO		
	<i>k</i> (min ⁻¹)	<i>R</i>	<i>t</i> _{1/2} (min)	<i>k</i> (min ⁻¹)	<i>R</i>	<i>t</i> _{1/2} (min)	<i>k</i> (min ⁻¹)	<i>R</i>	<i>t</i> _{1/2} (min)
Deionized water	0.0018	0.9976	387.59	0.0016	0.9955	443.85	0.0019	0.9989	364.81
Distilled water	0.0030	0.9985	228.38	0.0022	0.9993	320.41	0.0028	0.9975	250.53
Sea water	0.00046	0.9930	1501.42	0.00057	0.9803	1208.98	0.00114	0.9945	605.37

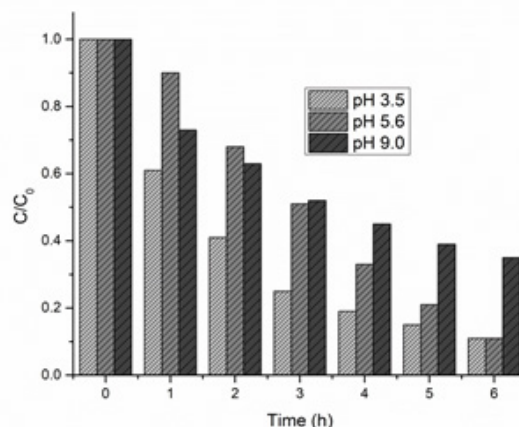


Figure 4. The effect of pH on the photocatalysis rate of methomyl under 366 nm (with 2 g/L of TiO₂, temperature 20 °C).

Degradation of 88.4 mg/L (4 x 10⁻⁴ M) of carbofuran and its commercial product Furadan 35-ST at 315-400 nm using 2 g/L of ZnO (Merck) catalyst was studied in order to assess the effects of inert ingredients present in the commercial product on carbofuran photodegradation. In order to be able to apply pesticides in agriculture, it is necessary to prepare them in the 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 containing the crucial active ingredient(s) and various other inert ingredients, depending on the formulation type. The inert ingredients may be: antifoam compounds, surfactants, solvents, antifreeze compounds, stability agents, carriers, dyes (occasionally), etc. [59-61]. Hence, the impact of the six inert ingredients present in Furadan 35-ST formulation (Tensiofix CD001, Tensiofix CP002, propylen glycol, polyacrylic acid, xanthan gum, and Rhodamin B) on the adsorption and photodegradation kinetics of carbofuran was examined comparatively. Differences in photodegradation rates were found significant over the first 15 min of degradation, which indicated a detrimental impact of inert ingredients present in the reaction medium containing Furadan 35-ST. Over the period of 15 min, the concentration of carbofuran decreased nearly 10 times, while carbofuran concentration in Furadan 35-ST decreased 2.9 times compared to initial concentration. The *k* value was higher for carbofuran degradation, 0.1072 min⁻¹, than for Furadan 35-ST, 0.0889 min⁻¹ (Table 5). Also, the ion chromatography results confirmed that mineralization of carbofuran and

Furadan 35-ST led to the formation of acetate, oxalate, and formate ions (detected in various relative concentrations) during the investigated processes (Figure 5), as well as to the formation of methylamine ion, CH₃NH₃⁺ [24]. In addition, GC-MS and HPLC-MS/MS analyses confirmed the formation of three photodegradation products of both carbofuran and Furadan 35-ST: carbofuran phenol, 3-hydroxycarbofuran, 3-ketocarbofuran phenol, and also two Furadan 35-ST degradation products: ion detected at *m/z* 240, (TP I), and ion detected at *m/z* 153 (TP II). GC-MS analysis revealed the presence of two carbofuran photocatalytic dimerization products: *m/z* 278 and 281 (*t_R* ≈ 16.18 and 18.05 min). Three degradation products (ions at *m/z* 153, 278, and 281) had not been previously reported [24].

Table 5. Pseudo-first-order rate constants of carbofuran and Furadan 35-ST at different pH values [24]

System	2.7		3.5		5.9		6.2		9.6		10.2	
pH	C	F	C	F	C	F	C	F	C	F	C	F
<i>k</i> (min ⁻¹)	0.1497	0.1047	0.1302	0.0994	0.1072	0.0889	0.0810	0.0737	0.0724	0.0710		
<i>R</i> ²	0.9890	0.9904	0.9654	0.9888	0.9836	0.9636	0.9584	0.9463	0.9786	0.9498		

C - Carbofuran

F - Furadan 35-ST

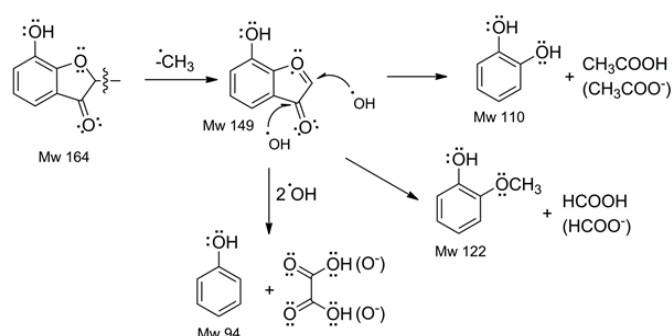
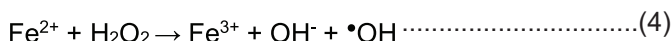


Figure 5. Characteristic fragmentation paths which explain the generation of formate, acetate, and oxalate ions in the course of photocatalytic degradation of carbofuran insecticide.

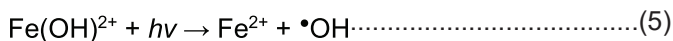
Photo-Fenton processes

Fenton and photo-Fenton processes have also received significant attention for water and wastewater treatments [19,62,63]. H.J.H. Fenton discovered in 1894 that several metals have special oxygen transfer properties which improve formation of hydrogen peroxide, i.e. some metals have a strong catalytic power to generate highly reactive hydroxyl radicals [64]. The classic Fenton's reagent is a mixture of ferrous ion and H₂O₂ in acidic solution or suspension [7, 19,65,66]:



Equation (4) presents the most important steps of a Fenton reaction and involves electron transfer between H₂O₂ and Fe²⁺ and the resulting production of the highly reactive hydroxyl radical •OH and potentially reactive Fe³⁺ species. Degradation of pesticides and other pollutants by Fenton's reagent can be strongly accelerated under UV or various types of visible light, including

sunlight. This process is named photo-Fenton reaction [19,22,34,66-69]. Equation (4) is the key of photo-Fenton processes. The obtained Fe³⁺ ion or its Fe(OH)²⁺ complexes act as light absorbing species, which produce another hydroxyl radical, while the initial Fe²⁺ ion is regained (equation 5), and the cycle continues [70]:



The great advantage of the photo-Fenton process, compared with heterogeneous photocatalysis with TiO₂ is its sensibility to light up to 600 (580) nm [68-70] and the photo-Fenton process allows a more efficient use of sunlight. Disadvantages of the photo-Fenton process include the aggressiveness of treatment due to the low pH required (usually below 4) and high consumption of H₂O₂. Both homogeneous and heterogeneous photo-Fenton processes may be performed. The contact between a pollutant and an oxidizing agent is more effective when the process occurs in homogeneous phase, but the need for removing iron at the end of the process is a disadvantage of its own. In homogeneous photo-Fenton reactions dissolved ferrous sulphate heptahydrate [66,69,71-73] or dissolved ferrous chloride hexahydrate [74] was used as a source of Fe²⁺ ions. The heterogeneous (when the reactant, products, and catalyst are in different phases) photo-Fenton process uses supported iron catalysts, such as Fe-ZSM-5 zeolite and AlFe-pillared montmorillonite (AlFe-PILC) [5, 11, 13, 14, 19, 75, 76]. These two catalysts have also been used for the destruction of other organic contaminants [77-80]. The kinetics of a photo-Fenton reaction depends on different factors, such as the initial reactant concentration and its characteristics, initial iron concentration and iron source, initial H₂O₂ concentration, pH, light intensity, and temperature [7, 11, 13, 14, 19].

The catalytic wet peroxide oxidation (heterogeneous photo-Fenton process) of water solution containing 16.22 mg/L of methomyl under halogen lamp light (λ= 575.6 nm) in a glass batch reactor under constant air flow, at room temperature and with two types of known iron supported catalysts (Fe-ZSM-5 zeolite and AlFe-pillared montmorillonite, i.e. AlFe-PILC) was performed [11, 13, 14, 19, 75, 76, 81]. The degradation rate of methomyl, and effect of two significant reaction parameters (initial pH and initial methomyl concentration) were also monitored. Fe-ZSM-5 at concentrations of 1 and 5 g/L, and AlFe-PILC catalyst at concentrations of 1, 3 and 5 g/L were used in the experimental study, which showed that methomyl degradation follows the pseudo-first-order reaction kinetics. (Table 6). Both applied catalysts showed a significant activity, but zeolite catalyst was superior. With 5 g/L of Fe-ZSM-5 the reaction was almost entirely completed within the first 30 min, while methomyl degradation with 1 g/L of the same catalyst continued for up to 4 h. The degradation of methomyl also proceeded when AlFe-PILC was used as the catalyst, but much more slowly than the reaction with zeolite. The advan-

tages of zeolite catalyst over pillared clay catalyst include higher activity, good stability (regarding retardation phenomena), and simple separation from the reaction mixture [78,81]. Degradation rate was influenced by the initial concentration of methomyl, and a positive effect of pH value (3.7) was also shown. The IC data showed that only sulfate, nitrate, and ammonium ions, at various concentrations, were formed and identified during degradation. Mineralization of organic carbon, sulfur, and nitrogen from the methomyl molecule was complete and degradation of methomyl practically finished in the first 30 min when 5 g/L of Fe-ZSM-5 zeolite was used, with 100% of TOC removal. Methomyl degradation under these conditions was extensive, without any intermediate compounds, and led to the formation of CO_2 , H_2O and inorganic ions (SO_4^{2-} , NH_4^+ , and NO_3^-). With 1 g/L of Fe-ZSM-5 zeolite, the reaction proceeded much slower

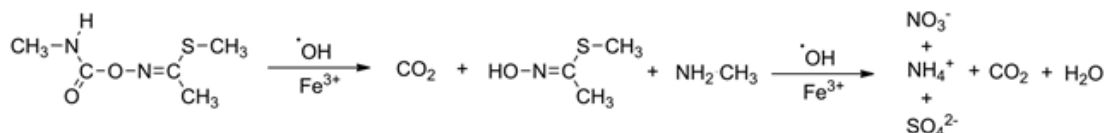


Figure 6. Tentative pathway for methomyl photocatalytic degradation in the presence of Fe-ZSM-5-zeolite (methomyl concentration 16.22 mg/L, catalyst concentration 1.0 g/L, pH 3.7).

The heterogeneous photo-Fenton reaction in methomyl and carbofuran water solutions (1.0×10^{-4} M) in a glass batch reactor at constant pH (3.5-4.0), in the presence of AlFe-pillared clay catalyst (PILC) and Fe-ZSM-5 zeolite catalyst (both 5.0 g/L), under halogen lamp light (575.6 nm) was investigated [76,82]. The applied catalysts decomposed methomyl successfully but were inactive for carbofuran degradation. Also, the catalyst testing of carbofuran conversion was carried out at both ambient and elevated (85 °C) temperature. Carbofuran could not be mineralized by the use of AlFe-PILC and Fe-ZSM-5 zeolite catalysts, even in a high-temperature catalytic reaction. The high chemical stability of the carbofuran molecule may be explained by its electronic structure, but this claim requires further theoretical and experimental investigations [76,82].

Conclusion

Photodegradation processes have been proposed as an effective and attractive techniques for degradation of carbamate pesticides methomyl and carbofuran in water. The kinetics of all photodegradation processes depends on several main parameters, such as the nature of pesticide, type of light, initial concentration of pesticides (and catalysts), pH of solution, temperature, and presence of an oxidant. The AOPs provide an excellent opportunity to use solar light as an energy source. The photochemical removal of methomyl and carbofuran is an applicable model for purification of water and wastewater.

than with 5 g/L of the same catalyst, and sulfate, nitrate, and ammonium ions, as well as methylamine, were obtained. In this case, mineralization of organic carbon was 80% within 240 min, and a tentative scheme of methomyl degradation was proposed (Figure 6) [19]. When AlFe-PILC catalyst was used, mineralization of methomyl solution led to the formation of sulfate, nitrate, and ammonium ions, too, but the process was incomplete [19].

Table 6. Pseudo-first-order rate constants of methomyl photodegradation in presence of AlFe-PILC and Fe-ZSM-5 catalysts [19]

Catalyst	AlFe-PILC	AlFe-PILC	AlFe-PILC	Fe-ZSM-5	Fe-ZSM-5
Concentration (g/L)	1	3	5	1	5
k (min^{-1})	0.0018	0.0020	0.0025	0.0147	0.0990
R^2	0.9727	0.9636	0.9007	0.9565	0.9045
Time (h)	0-8	0-8	0-8	0-4	0-0.5

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Izvod

FOTOHEMIJSKI PROCESI ZA UKLANJANJE KARBAMATNIH PESTICIDA IZ VODE

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U cilju zaštite bilja u svetu je registrovan i u prometu se nalazi veliki broj aktivnih materija pesticida. Većina pesticida, uključujući karbamate je otporna na hemijske i prirodne fotohemijske degradacije i zato je prioritet razvijanje odgovarajućih metoda za prečišćavanje zagađenih voda. Postoje različite metode za odstranjivanje ostataka karbamatnih pesticida iz vode a u ovom radu su razmatrane fotodegradacione metode. Prema literaturnim podacima najkorisniji fotohemijski procesi za uklanjanje pesticida iz vode su dva dobro poznata Viša oksidaciona procesa: heterogena fotokataliza u prisustvu poluprovodnih oksida TiO₂ i ZnO, i homogeni foto-Fenton postupak, isto kao i direktna ultraljubičasta fotoliza. Fotohemijska istraživanja doprinose boljem razumevanju ponašanja karbamatnih pesticida u životnoj sredini i puno informacija o vremenu degradacije aktivnih materija, njihovoj aktivnosti i sudbini u životnoj sredini može se dobiti proučavanjem kinetike svake fotohemijske reakcije.

Ključne reči: metomil, karbofuran, foto-degradacija, fotoliza, fotokataliza