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Photoremediation of Carbamate Residues in Water

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1. Introduction

Pesticides are extensively world wide used for agriculture and for non-agricultural purposes. The major environmental concern of used pesticides is their ability to leach down to subsoil and contaminate the ground water, or, if they immobile, they could persist on the top soil and become harmful to microorganisms, plants, animal and people (Jha & Mishra 2005; Radivojević et al., 2008). Harmfull pesticide residues can contaminate the environment and accumulate in ecosystems than entering the human food chain (Đurović et al., 2010; Gašić et al., 2002a; Gevao et al., 2000). Pesticides have various characteristics that determine how act once in soil where it could accumulate to toxic level. Generally, soil and groundwater pollution are the major consequences environmental effects of pesticides application. Pesticides can reach water through surface runoff from treated plants and soil. Pesticide sprays usually directly hit non-target vegetation or can drift or volatilize from the treated areas that contaminate air, soil, and non-target plants. Finally, using of pesticides has resulted in acute and chronic ecological damage either by direct injury such as birds and fish or by indirect.

Carbamates are large group of pesticides which have been extensively used in almost sixty years. In this chapter an attempt is made to give the available data of the carbamates used as pesticides, their physico-chemical and toxicological characteristics, behaviour and fate in the environment, types of formulations which exist on the market as well as photochemical degradation for the certain members. Owing to widespread use in agriculture and relatively good solubility in water carbamate compounds can contaminate surface and ground waters and therefore carries a risk to various consumers, as well as the environment.

In this chapter we will also discuss some very important photocatalytic methods for remediation of water containing carbamate residues: direct photodegradation (photolysis), photosensitized degradation and photocatalytic degradation (including heterogeneous TiO_2 and ZnO processes and photo-Fenton and Fenton-like processes).

2. Carbamates

Carbamates were developed into commercial pesticides in the 1950s. It is a very huge family which members are effective as insecticides, herbicides, and fungicides, but they are most commonly used as insecticides. More than 50 carbamates are known. The most often used

members of carbamate group are: aldicarb, asulam, bendiocarb, carbaryl, carbetamid, carbofuran, carbosulfan, chlorpropham, desmedipham, ethiofencarb, formetanate, furatiocarb, fenoxycarb, isoprocarb, methiocarb, methomyl, oxamyl, phenmedipham, pirimicarb, promecarb, propamocarb and propoxur.

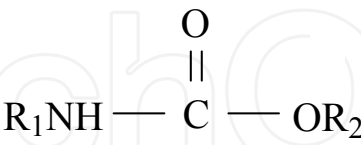Carbamates are N-substituited esters of carbamic acid. Their general formula is:

$$R_1NH - \overset{\overset{\displaystyle O}{\displaystyle \|}}{C} - OR_2$$

Fig. 1. General carbamate structure, where R_2 is an aromatic or aliphatic moiety, if R_1 is a methyl group it is carbamate insecticide, if R_1 is an aromatic moiety it is carbamate herbicide and if R_1 is a benzimidazole moiety it is carbamate fungicide (WHO, 1986).

Pesticide activity	Chemical structure	Common or other names
Insecticide	$CH_3 - NH - \overset{\overset{O}{\|}}{C} - O - aryl$	aldoxycarb, allyxycarb, aminocarb, BPMC, bendiocarb, bufencarb, butacarb, carbanolate, carbaryl, carbofuran, cloethocarb, dimetilan, dioxacarb, ethiofencarb, formetanate, hoppcide, isoprocarb, trimethacarb, MPMC, methiocarb, metolcarb, mexacarbate, pirimicab, promacyl, promecarb, propoxur, MTMC, XMC, xylylcarb
	$CH_3 - NH - \overset{\overset{O}{\|}}{C} - O - N - alkyl$	aldicarb, methomyl, oxamyl, thiofanox, thiodicarb
Herbicide	$aryl - NH - \overset{\overset{O}{\|}}{C} - O - alkyl$	asulam, barban, carbetamide, chlorbufam, desmedipham, phenmedipham, swep
	$alkyl - NH - \overset{\overset{O}{\|}}{C} - O - aryl$	dichlormate, karbutilate, terbucarb
Herbicide and sprout inhibitors	$aryl - NH - \overset{\overset{O}{\|}}{C} - O - alkyl$	propham, chlorpropham
Fungicide	$aryl - NH - \overset{\overset{O}{\|}}{C} - O - alkyl$	benomyl, carbendazim, thiophanate-methyl, thiophanate-ethyl

Table 1. Relationship of chemical structure and pesticide activity of carbamates (WHO, 1986).

2.1 Carbamates physical and chemical properties

It is known that esters or N-substituted derivates of carbamic acid are unstable compounds, especially under alkaline conditions. Decomposition under this conditions takes place and the compounds as alcohol, phenol, ammonia, amine and carbon dioxide are formed.

Derivates of carbamic acid as salts or esters are more stable than carbamic acid. This enhanced stability is the basis for synthesis of many derivates that are biologically active pesticides.

Carbamate ester derivates are crystalline solids of low vapor pressure with variable, but usually low water solubility. They are moderately soluble in solvents such as benzene, toluene, xylene, chloroform, dichloromethane and 1,2-dichloromethane. Generally, they are poorly soluble in nonpolar organic solvents such as petroleum hydrocarbons but highly soluble in polar organic solvents such as methanol, ethanol, acetone, dimethylformamide, etc (WHO, 1986).

2.2 Carbamates mode of action and toxicity

Most carbamates are active inhibitors of acetylholinesteraze (AChE), but some carbamates as benzimidazole have no acetylcholinesterase activity. Carbamates toxicity to insects, nematodes, and mammals is based on inhibition of acetylcholinesterase, which is the enzyme responsible for the hydrolysis of acetycholine into choline and acetic acid. Acetylcholine (ACh) is a substance that transmits a nerve impulse from a nerve cell to a specific receptor such as another nerve cell or a muscle cell. Acetylcholine, in essence, acts as a chemical switch. When it is present (produced by nerve cell) it turns the nerve impulse on. When it is absent, the nerve impulse is discontinued. The nerve transmission ends when the enzyme aceylcholinesterase breaks down the acetylcholine into choline and acetic acid. Without the action of this enzyme acetylcholine builds up at the junction of nerve cell and the receptor site, and the nerve impulse continues. Carbamate insecticides block (or inhibit) the ability of this enzyme, acetylcholinesterase, to break down the acetylcholine and the nerve impulse (Kamrin, 1997; Machemer & Pickel, 1994).

In mammals, cholinesterase inhibition caused by carbamates is labile, reversible process. Estimates of the recovery time in humans range from immediate up to four days, depending on the dose, the specific pesticide and the method of exposure. The breakdown of carbamate compounds within an organisms is a complex process and is depended on the specific pesticide structure. The rapid degradation of carbamates *in vivo* by mammals occurs by hydrolysis, oxidation and conjugation. The end products include amines, alcohols or phenol derivates. The urinary route is the main excretory route (Machemer & Pickel, 1994).

Inhibition of acetylholinesteraze (AChE) by carbamates causes toxic effects in animals and human beings that result in variety of poisoning symptoms. Carbamates acute toxicity and poisoning are dose related. Acute poisoning occurs rapidly after exposure. Ingestion of carbamate insecticides at low doses can cause excessive salivation and an increase in the rate of breathing within 30 min. At higher doses this is followed by excessive tearing, urination, no control defecation, nausea and vomiting. At the highest doses, symptoms can include those listed above along with violent intestinal movements, muscle spasm and convulsions. Death has occurred in a few instances, usually due to respiratory failure resulting from paralysis of the respiratory muscles (Kamrin, 1997; WHO, 1986).

While the insecticidal carbamate produce the typical symptoms of cholinesterase inhibition, they don't appear to induce a delayed neurotoxic reaction similar to that seen with some organophosphourus compound. Chronic exposure to carbamate compounds may cause

adverse effects on organs or acetylcholinesterase levels. These effects are unlikely to occur in humans at expected exposure levels (Kamrin, 1997).

The acute toxicity of different member of carbamates ranges from highly toxic to only slightly toxic. The LD_{50} for the rats ranges from less than 1 mg/kg to over 5000 mg/kg body weight. The acute dermal toxicity of carbamates is generally low to moderate except aldicarb which is very toxic. The carbamates in short term and long term toxicity studies showed different toxicity. Some carbamates are very toxic and others less. Carbamate pesticides are transformed metabolically by variety of chemical reactions in more water soluble molecules which can be excreted via the urine. Rats eliminate carbamate compounds rapidly in that way. Most metabolites are excreted within 24 h of exposure and therefore carbamate residues don't accumulate in animals (Kamrin, 1997; WHO, 1986). In the study of carbofuran toxicity on rats during subhronic exposure the histopathological changes in liver and kidneys were observed but there was cell regeneration in all test groups as well (Brkić et al., 2008).

Aldicarb is the most toxic among the carbamates and establish acceptable daily intake (ADI) for humans is 0.001 mg/kg/body weight. The other carbamates have ADIs values in range of 0.001-0.1 mg/kg/ body weight (WHO, 1986). According to the European Food Safety Authority (2009), the lowest ADI has carbofuran 0.00015 mg/kg/body weight (EU Pesticide Database, 2011).

Many carbamates have been studied for reproductive, teratogenic, mutagenic and carcinogenic effects and the results of this is that a few members of this family has been banned by the regulatory bodies worldwide.

2.3 Environmental fate

Generally, carbamates remain active for a few hours to a few month in soils and crop, but they may leave residues in agricultural products (Takino et al., 2004). The rate of degradation in soil depends on soil type, soil moisture, adsorption, pH, soil temperature, concentration of pesticide, microbial activity and photodecomposition. The higher the organic content, the greater the binding to soil and thus the greater the persistence. Also, the higher the soil acidity, the longer it takes for carbamates to be degraded. Carbamate insecticides are mainly applied on the plants, but can reach the soil, while carbamate nematocides and herbicides are applied directly to the soil. Generally, in soil carbamates degraded by chemical hydrolysis and microbial processes. Microorganisms that have capability to degrade carbamate pesticides play a significant role in the break dawn and elimination of them from environment. Because the different carbamates have different properties, it is clear that each of them should be evaluated on its own merits, and no extrapolation of results can be made from one carbamate to another. One carbamate may be easily decomposed, while another may be strongly adsorbed on soil. Some leach out easily and may reach groundwater. In these processes, the soil type and water solubility are of great importance. Furthermore, it should be recognized that this not only concerns the parent compound but also the breakdown products or metabolites (Kamrin, 1997; WHO, 1986).

Persistence of carbamate herbicides is increased by application to dry soil surface or by soil incorporation. Environmental factors which increasing microbial activity in soil generally decrease the persistence of carbamate herbicides. In most of degradation reactions the initial cleavage of the molecule occurs at ester linkage. Enzymatic hydrolysis of some carbamates can be correlated to soil acidity, and rate differences explained by consideration of certain

steric and electronic properties of the carbamates. The carbamate derivates with herbicidal action are substantially more stable to alkaline hydrolysis than the methyl carbamate derivatives, which have an insecticidal action (Kaufman, 1967).

Carbamate compounds degrade through chemical hydrolysis and this is the first step in the metabolic degradation. The hydrolysis products will be further metabolized in soil and plant. Chemical degradation does not appear to have much influence in the total degradation of pesticides in soil. Carbamate compounds are adsorbed and translocated through plants and treated crops. In most cases, carbamates will break down quickly in plants and the residues in plants will last not very long .

Finally carbamates are metabolized by microorganisms, plants and animals or broken down in water or soil. In water carbamates degraded by chemical hydrolysis, but photodegradation and aquatic microbes may also contribute degradation. Generally, in alkaline water and under sunlight carbamate compounds will decompose more rapidly (WHO, 1986).

2.4 Formulations

Carbamate products come in variety of solid and liquid formulations on the market. They contain beside carbamate compounds inert ingredients which could be toxic, flammable or reactive. Examples of inert ingredients are wetting agents, spreaders, dispersing agents, solvents, solubilizers, carriers, ticker, surfactants and so on. A surfactant is a substance that reduced surface tension of a system, allowing oil-based and water-based substances to mix more readily. A common groups of non-ionic surfactants are the alkylphenol polyethoxylates or alcohol ethoxylates which may be used in pesticide formulations. Nonyl phenols, one of the members of above mention alkylphenol surfactant has been linked to endocrine-disrupting effects in aquatic animals and should be substituted by less hazardous alternatives. Commonly used formulation types include liquid and dry formulations as emulsifiable concentrates (EC), soluble concentrates (SL), suspension concentrates (SC), than wettable powders (WP), water dispersible granules (WG), granules (GR), etc, and they are signed by international coding system (CropLife, 2008).

Pesticides are very often formulated as emulsifiable concentrates (EC) which produce emulsions when dissolved in water. The first problem in defining this formulation is the selection of an adequate surfactants (emulsifiers) for the intended purposes (Gašić et al., 1998a, 1998b, 2002b; Shinoda & Friberg, 1986). Recently there is increasing interest in the effect of emulsifiers on toxicity to mammals and fish. These effects can be due to inherent toxicity of the surfactant itself or to the enhancing effect that the emulsifiers may have on toxicity of active ingredient. So, the formulation type can have implications for product efficacy and exposure to humans and other non-target organisms (Knowles, 2005, 2006; Sher, 1984).

While the toxicity of the active ingredient of a pesticide is property which can not be changed, the acute toxicity effects of the formulation are strongly influenced by the way in which the active ingredient is formulated. While pesticide formulations are influenced by both the physical and chemical properties of the active ingredient and the economic pressures of the marketplace, there are formulation choices which will increase the safety of pesticide formulations (Mollet & Grubenmann, 2001).

The type of pesticide formulations and in, some cases, the choice of product of the same formulation type can significantly affect the results obtained in practical use. Safety, efficacy, residual life, cost, availability and ease of use must all be considered in selecting

formulation. The ways in which pesticides are formulated considerably influence their persistence. Formulations in order of increasing persistence on plants are prepared in the way that more readly adsorbed on the soil fractions and not appreciably degradated (Edwards, 1975).

3. Photodegradation processes for carbamates wastewater treatments

3.1 Photolysis

Photolysis (direct photodegradation reaction) is photodegradation process without any catalysts and use light only for degradation of different organic molecules, including pesticides and related compounds. Direct irradiation will lead to the promotion of the pesticides to their excited singlet states and such excited states can then undergo among homolysis, heterolysis or photoionization processes (Burrows et al., 2002). Direct photodegradation by solar light is limited and various lamps have been used for irradiation of contaminated water solutions. The photolysis of contaminants (including pesticides) in aqueos solution depends on the different 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 (Burrows et al., 2002; Tomaševic at al., 2010a).

3.2 Photosensitized degradation

The photosensitized reaction is based on the absorption of light by a molecule of the sensitizer and includes an energy transfer from molecul excited state to the pesticides. The most famous sensitizers are aceton, rose Bengal, methylene blue and humic and fulvic acids (Burrows et al., 2002).

3.3 Advanced oxidation processes

Advanced Oxidation Processes (AOPs) include catalytic and photochemical methods and have H_2O_2, O_3 or O_2 as oxidant. The principal active species in this system is the hydroxyl radical $^\bullet$OH, which is an extremely reactive and non-selective oxidant for organic contaminants (Legrini at al., 1993; Sun & Pignatello, 1993). The main advantage of these processes is a complete mineralization of many organic pollutants (Andreozzi at al., 1999; Neyens & Baeyens, 2003). Several of AOPs are currently employed for the elimination of pesticides from water: heterogeneous photocatalytic reactions with semiconductor oxides TiO_2 (Malato et al., 2002a, 2002b; Tomaševic at al., 2010a) or ZnO (Tomaševic at al., 2010a) as photocatalysts, photo-Fenton (Malato et al., 2002a; Tamimi et al, 2008; Tomaševic at al., 2010b) and photo-assisted Fenton processes (Huston & Pignatello, 1999). Electro-photo-Fenton (Kesraoui Abdessalem et al., 2010) and electrochemical oxidation processes (Tomašević et al., 2009a) have been seldom studied.

Heterogeneous photocatalysis is combination of semiconductor particles (TiO_2, ZnO, Fe_2O_3, CdS, ZnS), UV/solar light and different oxidants (H_2O_2, $K_2S_2O_8$, KIO_4, $KBrO_3$). The main equations of the heterogeneous photocatalysis are (Andreozzi et al., 1999; Daneshvar et al., 2003; Karkmaz et al., 2004; Legrini at al., 1993):

$$C + h\nu \rightarrow C\,(e^- + h^+) \tag{1}$$

$$h^+ + H_2O \rightarrow {}^\bullet OH + H^+ \tag{2}$$

$$e^- + O_2 \rightarrow O_2^{\bullet-} \tag{3}$$

Among AOP$_s$, heterogeneous photocatalysis using TiO$_2$ as photocatalyst appears as the most emerging destructive technology. The following mechanism of the TiO$_2$ photocatalysis has been proposed (Daneshvar et al., 2003; Gomes da Silva & Faria, 2003; Karkmaz et al., 2004; Tomaševic at al., 2010a):
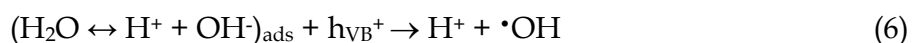
a) absorption of efficient photons by titania ($h\nu \geq$ Eg=3.2 eV):

$$TiO_2 + h\nu \,(UV) \rightarrow e_{CB}^- + h_{VB}^+ \tag{4}$$

b) oxygen ionosorption:

$$(O_2)_{ads} + e_{CB}^- \rightarrow O_2^{\bullet-} \tag{5}$$

c) neutralization of OH$^-$ groups into $^\bullet$OH by photoholes:

$$(H_2O \leftrightarrow H^+ + OH^-)_{ads} + h_{VB}^+ \rightarrow H^+ + {}^\bullet OH \tag{6}$$

d) oxidation of the organic reactant via successive attacks by $^\bullet$OH radicals:

$$R + {}^\bullet OH \rightarrow R'^\bullet + H_2O \tag{7}$$

e) or by direct reaction with holes:
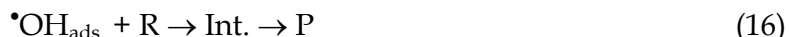
$$R + h^+ \rightarrow R^{\bullet+} \rightarrow \text{degradation products} \tag{8}$$

ZnO is also frequently used as a catalyst in heterogeneous photocatalytic reactions. The biggest advantage of ZnO in comparison to TiO$_2$ is that it absorbs over a larger fraction of the UV spectrum and the corresponding threshold wavelength of ZnO is 387 nm. Upon irradiation, valence band electrons are promoted to the conduction band leaving a hole behind. These electron-hole pairs can either recombine or interact separately with other molecules. The holes at the ZnO valence band can oxidize adsorbed water or hydroxide ions to produce hydroxyl radicals. Electron in the conduction band at the catalyst surface can reduce molecular oxygen to superoxide anion. This radical may form organic peroxides or hydrogen peroxide in the presence of organic scavengers. The hydroxyl radical attacks organic compounds (R) and intermediates (Int) are formed. These intermediates react with hydroxyl radicals to produce the final products (P). The mechanism of heterogeneous photocatalysis in the presence of ZnO can be given by the following reactions (Behnajady et al., 2006; Daneshvar et al., 2004, 2007; Pera-Titus at al,. 2004; Tomaševic at al., 2010a):

$$ZnO + h\nu \,(UV) \rightarrow e_{CB}^- + h_{VB}^+ \tag{9}$$

$$e_{CB}^- + h_{VB}^+ \rightarrow \text{heat} \tag{10}$$

$$h_{VB}^+ + H_2O_{ads} \rightarrow H^+ + {}^\bullet OH_{ads} \tag{11}$$

$$h_{VB}^+ + {}^- OH_{ads} \rightarrow {}^\bullet OH_{ads} \tag{12}$$

$$e_{CB}^- + O_2 \rightarrow O_2^{\bullet-} \tag{13}$$

$$O_2^{\bullet-} + HO_2^\bullet + H^+ \rightarrow H_2O_2 + O_2 \tag{14}$$

$$O_2^{\bullet -} + R \rightarrow R\text{-}OO^{\bullet} \tag{15}$$

$$^{\bullet}OH_{ads} + R \rightarrow Int. \rightarrow P \tag{16}$$
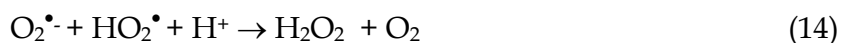
Fenton′s processes belong to AOP$_s$ and utilize H_2O_2 activation by iron salts. The classic Fenton′s reagent is a mixture of ferrous ion and H_2O_2 in acidic solution or suspension (Neyens & Baeyens, 2003; Tamimi at al.,2008):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {\bullet}OH \tag{17}$$

Equation (17) presents the most important steps of a Fenton reaction and involves electron transfer between H_2O_2 and Fe(II) with oxidation of Fe(II) to Fe(III) and the resulting production of highly reactive hydroxyl radical ${\bullet}OH$ and potentially reactive ferryl species. The degradation of pesticides by Fenton′s reagent can be strongly accelerated upon UV or UV-visible light. This process is the photo-Fenton reaction (Malato et al., 2002a, 2002b; Tamimi et al, 2008; Tomašević at al., 2010b). Equation (17) is the key of photo-Fenton processes. The obtained Fe^{3+} ion or its Fe(OH)$^{2+}$ complexes act as light absorbing species, that produce another hydroxyl radical, while the initial Fe^{2+} ion is regained:

$$Fe(OH)^{2+} + hv \rightarrow Fe^{2+} + {\bullet}OH \tag{18}$$

The main advantage of the photo-Fenton process is light sensitivity up to a wavelength of 600 nm (Malato et al., 2002a).

4. Photodegradation of carbamate pesticides

4.1 Aldicarb

Aldicarb (IUPAC name: 2-methyl-2-(methylthio)propionaldehyde O-methylcarbamoy-oxime) is a systemic oxime carbamate pesticide, effective against a variety of insects, mites, and nematodes. It is sold commercially only in granular form (GR). Aldicarb is applied on a variety of crops, including cotton, sugar beet, sugarcane, citrus fruits, potatoes, sweet potatoes, peanuts, beans (dried beans), soybeans, pecans, and ornamental plants. Home and garden use is not permitted in many countries. The current regulation status of this active ingredient under directive 91/414/EEC is not included in Annex 1 (EU Pesticide Database, 2011; Tomlin, 2009).

The complete conversion of 38 mg/L of aldicarb and 62% reduction in TOC content using the photo-Fenton reaction (Fe(III)/H$_2$O$_2$/UV) within 120 min in acidic aqueous solution (pH 2.8) at 25 °C with fluorescent blacklight irradiation (300-400 nm) has been considered (Huston & Pignatello, 1999). They also observed the formation of sulfate and nitrate ions during the photo-Fenton process.

4.2 Asulam

Asulam (IUPAC name: methyl sulanylcarbamate) is selective systemic herbicide, which is used for control of annual and perennial grasses and broad-leaved weeds in spinach, oilseed poppies, alfalfa, some ornamentals, sugar cane, bananas, coffee, tea, cocoa, coconuts, rubber, fruit trees and bushes, and forestry. It could be found only as soluble concentrate (SL) on the market. The current regulation status of this active ingredient under directive 91/414/EEC is not included in Annex 1 (EU Pesticide Database, 2011; Tomlin, 2009).

The degradation of asulam was studied in homogeneous aqueous solution in the presence of molecular oxygen at pH 3.0-3.4, by irradiation at 365 nm and by solar irradiation (Catastini et al., 2002a). When the iron(III) aquacomplexes was photoreduced to iron(II) ions and hydroxyl radicals the degradation of asulam in the presence of oxygen continud to completion. The Fe^{2+} ions are oxidized back to Fe^{3+} ions through various pathways such as photooxidation and oxidation by H_2O_2 generated within the system, where another $^\bullet OH$ forms. Their experimental results indicate that the presence of Fe^{3+}, Fe^{2+} and molecular oxygen accelerate the mineralization of asulam. Also, less than 10% conversion of asulam was observed when the irradiation was performed in the presence of 0.01 M 2-propanol, used as hydroxyl radical scavenger. Complete conversion and nearly complete TOC reduction of 23 mg/L of asulam was achieved with 16.7 mg/L of Fe^{3+} ions, within 17 h (at 365 nm) and 28-30 h (under solar light). In this process intermediates or degradation by-products of asulam were not identified. The photodegradation of the herbicide asulam in aqueous solution (1.0×10^{-4} M or 23 mg/L) has been investigated with and without Fe(III) (Catastini et al., 2002b).The asulam disappearance were monitored by photolysis at 254 nm as a functuion of pH and oxygen concentration and no complete transformation of organic carbon into CO_2 was observed. In the presence of Fe(III) at 365 nm the complete mineralization of asulam has been achieved.

4.3 Bendiocarb

Bendiocarb (IUPAC name: 2,3-isopropyldenedioxyphenyl methylcarbamate, 2,2-dimethyl-1,3-benzodioxol-4-yl methylcarbamate) is systemic insecticide with contact and stomach action. It is active against many public health, industrial and storage pest. This active ingredient is especially useful inside buildings, due to its low odor and lack of corrosive and staining properties. It comes in variety formulations type as DP, FS, GR, SC, WP on the market. The current regulation status of this active ingredient under directive 91/414/EEC is not included in Annex 1 (EU Pesticide Database, 2011; Tomlin, 2009).

Evaluation of different pathway (photolysis, photo-Fenton, H_2O_2/UV and electro-Fenton) of bendiocarb (112-188 mg/L) photodegradation have been proposed (Aaron & Oturan, 2001). The conversion of insecticide was apparently much faster in the H_2O_2/UV and photo-Fenton proces ($\lambda = 254$ nm, 68 mg/L of H_2O_2 and 55.8 mg/L of Fe^{3+}) than in the other processes. Also, the degradation mechanism of bendiocarb has been proposed. The photolysis of aqueous bendiocarb (3.3×10^{-3} M, 4 h, room temperature, 125 W medium-pressure mercury lamp) has been examined by GC-MS (Climent & Miranda, 1996). Upon irradiation the only one photo-product (corresponding phenol) was detected and 30% conversion of bendiocarb was achieved.

4.4 Carbaryl

Carbaryl (IUPAC name: 1-naphthyl methylcarbamate) is insecticide with contact and stomach action and has slight systemic properties. It is used for control of chewing and sucking insects on more than 120 different crops, including vegetables, tree fruit (including citrus), mangoes, bananas, strawberries, nuts, vines, olives, okra, cucurbits, peanuts, soya beans, cotton, rice, tobacco, cereals, beet, maize, sorghum, alfalfa, potatoes, ornamentals, forestry, etc, than for control earthworms in turf and as a growth regulator for fruit thinning of apples. Also it is used against an animal ectoparasiticide. Carbaryl can be found formulated as DP, GR, OF, RB, SC, TK and WP. The current regulation status of this active

ingredient under directive 91/414/EEC is not included in Annex 1 (EU Pesticide Database, 2011; Tomlin, 2009).

The degradation of carbaryl under UV light using a continuous flow of TiO_2 slurry shown that the degradation proceeds through a multi-step process involving the attack of the substrate by $^{\bullet}OH$ radicals (Peris at al., 1993). The studies on the degradation of carbaryl under simulated solar light in aqueous TiO_2 dispersions showed that the reaction follows pseudo-first-order kinetics and the complete mineralization (to CO_2, nitrate and ammonium ions) is achieved in less 30 min (Pramauro et al., 1997). The effect of ionic and non-ionic aliphatic surfactants (constitute an important ingredient of pesticide formulations and can influence the degradation of pesticide) on the degradation of aqueous carbaryl solutions (20 mg/L) containing 500 mg/L of TiO_2 (anatase) in the presence of simulated solar light (1500 W Xenon lamp with 340 nm cut-off filter) was investigated (Bianco Prevot at al., 1999). Depending on the surfactant and on the initial pH of the solution, an inhibition ot the photodegradation rate was observed. Also, mineralization of the carbaryl to CO_2, nitrate and ammonium ions was evidence in the presence of added surfactants, suggesting the feasibility of photocatalytic treatment of aqueous pesticide wastes.

4.5 Carbetamid

Carbetamid (IUPAC name: (R)-1-(ethylcarbamoyl)ethyl carbamilate) is selective herbicide, absorbed by the roots, and also by the leaves. It is used for control of annualgrasses and some broad-leaved weeds, alfalfa, sainfoin, brassicas, field beans, peas, lentils, sugar beast, oilseed rape, chicory, endive, sunflowers, caraway, strawberries, wines, and fruit orchards. Formulations types for this active ingredient are EC and WP. The current regulation status of this active ingredient under directive 91/414/EEC is included in Annex 1, expiration of inclusion: 31/05/2021 (EU Pesticide Database, 2011; Tomlin, 2009).

Photodegradation of herbicide carbetamide with ultraviolet light ($\lambda > 290$ nm) in the presence of TiO_2, H_2O_2 and ozone was studied in the aqueous solutions (Mansour et al., 1992). Using spectrometric methods several photoproducts were isolated and identified, suggesting that photodegradation pathways of carbetamide in the presence of TiO_2 and H_2O_2 are hydroxylations of the aromatic ring. Also, UV-ozonation rapidly oxidized carbetamide to water, ammonia and CO_2. The kinetics of photodegradation of carbetamide in water in the presence of TiO_2 (Degussa P 25 grade, surface area 50.0 m^2/g) or ZnO (surface area 9.5 m^2/g) were examined upon $\lambda \geq 310$ nm (Percherancier et al., 1995). The effects of various parameters, such as the kind of semiconductor, mass of TiO_2, initial concentration of pesticide, radiation flux and quantum yield were studied. The degradation with ZnO is faster than that with TiO_2 in spite of the lager surface area of the later catalyst. Also, the mechanism of the carbetamide photocatalytic degradation has been proposed.

4.6 Carbofuran

Carbofuran (IUPAC name: 2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate) is systemic insecticide with predominantly contact and stomach action. It is used for control of soil-dwelling and foliar-feeding insects and nematodes in vegetables, ornamentals, beet, maize, sorghum, sunflowers, oilseed rape, potatoes, alfalfa, peanuts, soya beans, sugar cane, rice, cotton, coffee, cucurbits, tobacco, lavender, citrus, wines, strawberries, bananas, mushrooms and other crops. This active ingredient is prepared as FS, GR, SC and WP formulation. The current regulation status of this active ingredient under directive 91/414/EEC is not included in Annex 1 (EU Pesticide Database, 2011; Tomlin, 2009).

Various carbofuran photodegradation processes (by ozon, UV photolysis, Fenton, O_3 + UV, UV + H_2O_2 and photo-Fenton) upon polychromatic UV irradiation were evaluated (Benitez et al., 2002). For all these reactions, the apparent pseudo-first–order rate constants are evaluated in order to compare the efficiency of each process. The most effective process in removing carbofuran from water was the photo-Fenton system (UV + Fe^{2+} + H_2O_2) with rate constants k from 17.2×10^{-4}/s to $>200.0 \times 10^{-4}$/s. The degradation of pure carbofuran and commercial product Furadan 4F in acidic aqueous solution upon polychromatic light (300-400 nm) by photo-assisted Fenton process has been studied (Huston & Pignatello, 1999). The complete conversion of 2.0×10^{-4} M of pure carbofuran and more than 90% TOC reduction in the water solution within 120 min has been achieved. Nitrate and oxalate ions were detected as organic ionic species after the treatment. Also, the results show that the adjuvants in Furadan 4F have little or no influence on degradation of carbofuran nor of TOC mineralization. Two different Advanced oxidation processes (photo- and electro-Fenton) have been used for photodegradation of carbofuran in water (Kesraoui Abdessalem et al., 2010). For the photo-Fenton process TOC removal ratio was influenced by the initial concentration of the pesticides and the amout of Fe^{3+} and H_2O_2. The TOC measurement indicate an efficient mineralization of 93 and 94% respectively, for photo- and electro-Fenton processes after 480 min of treatment. Carbofuran could not be mineralized on AlFe-PILC and Fe-ZSM-5 zeolite catalysts in the heterogeneous photo-Fenton reactions at 575.6 nm, even in the catalytic reaction promoted at high temperature (Tomašević et al., 2007a, 2007b).

4.7 Ethiofenocarb

Ethiofencarb (IUPAC name: $\propto$-ethythio-$\propto$-tolyl methylcarbamate) is systemic insecticide with contact and stomach action. It is applied for control of aphids on pome fruit , stone fruit and soft fruit, than vegetables, ornamentals and sugar beet. Formulations types which can be found on the market are: emulsifieble concentrate (EC), emulsions oil in water (EW) and granules (GR). The current regulation status of this active ingredient under directive 91/414/EEC is not included in Annex 1 (EU Pesticide Database, 2011; Tomlin, 2009).

Solar photodegradation of ethiofencarb was examined in pure water, natural water and in the pure water containing 10mg/L of humic acids (Vialaton & Richard, 2002). Photosensitized reactions are main degradation pathway of pesticide in natural water and in the presence of humic acids. Photosensitized transformations were shown to be largely due to photoreactants other than singlet oxygen and hydroxyl radicals. A comparative photolysis reactions of ethiofencarb in water and non-water media were performed in the presence of simulated solar light (Sanz-Asensio et al., 1999). The studies showed that the photolysis reaction follows pseudo-first-order kinetics and that the degradation kinetics depend on the solvent polarity. In the water media the reaction of pesticide degradation was completed for 30 h. Also, the photoproducts are dependent on the solvent and the main photoproduct in water was 2-(methyl)phenyl-N-methylcarbamate. The photolysis of aqueous ethiofencarb (3.3×10^{-3} M, 4 h, room temperature, 125 W medium-pressure mercury lamp) has been examined by GC-MS (Climent & Miranda, 1996). Upon irradiation three photoproducts were detected and 66% conversion of ethiofencarb was achieved. The main product was 2-methylphenyl methylcarbamate, and two corresponding phenols also were registered.

4.8 Formetanate

Formetanate (IUPAC name: 3-dimethylaminomethyleneaminophenyl methylcarbamate) is acaricide and insecticide with contact and stomach action. It is used for control of spider mites and some insects on ornamentals, pome fruit, stone fruit, citrus fruit, vegetables and alfalfa. It is sold commercially only as soluble powder (SP). The current regulation status of this active ingredient under directive 91/414/EEC is included in Annex 1, expiration of inclusion: 30/09/2017 (EU Pesticide Database, 2011; Tomlin, 2009).

The solar driven photo-Fenton process using pilot-scale compound parabolic collector was applied to the degradation of formetanate in the form of AgrEvo formulated product Dicorzol (Fallman et al., 1999). The results shown that a good conversion of formetanate was achieved (about 25 min was a TOC half-life and about 70 min was the time necessary for degradation of 80% of TOC). The heterogeneous photocatalysis with TiO_2 (200 mg/L) and homogeneous photocatalysis by photo-Fenton (0.05 mM of $FeSO_4 \times 7H_2O$) of 50 mg/L of formetanate have been studied (Malato et al., 2002b). In the presence of 2.8 mg/L of Fe^{2+} complete conversion of formetanate and more than 90% TOC reduction was demonstrated in pilot-scale solar reactor. The kinetics of formetanate degradation by the TiO_2 solar photocatalysis and by the solar photo-Fenton process were also investigated (Malato et al., 2002b, 2003).

4.9 Methomyl

Methomyl (IUPAC name: S-methyl N-(methylcarbamoyloxy)thioacetimidate) is systemic insecticide and acaricide with contact and stomach action. It is used for control of a wide range of insects and spider mites in fruit, vines, olives, hops, vegetables, ornamentals, field crops, cucurbits, flax, cotton, tobacco, soya beans, etc. Also it can be used for control of flies in animal and poultry houses and dairies. Formulations types for this active ingredient are SL, SP, WP. The current regulation status of this active ingredient under directive 91/414/EEC is included in Annex 1 expiration of inclusion: 31/08/2019 (EU Pesticide Database, 2011; Tomlin, 2009).

The solar driven homogeneous photo-Fenton and heterogeneous TiO_2 processes for methomyl detoxification in water have been evaluated (Malato et al., 2002b, 2003). According to TOC removal, the photo-Fenton process was more efficient in degrading 50 mg/L of methomyl than was the TiO_2 process. The both processes were capable of mineralizing more than 90% of the insecticide (Malato et al., 2002b). The photodegradation of methomyl by Fenton and photo-Fenton reactions were investigated (Tamimi et al., 2008). The degradation rate and the effect of reaction parameters (initial concentration of pesticide, pH, ferrous and H_2O_2 dosage, etc) were monitored. The photo-Fenton was more efficient than Fenton, both for methomyl degradation and TOC removal. The catalytic wet peroxide oxidation of methomyl at 575.6 nm (photo-Fenton reaction) with two types of heterogeneous iron catalysts (Fe-ZSM-5 zeolite and AlFe-pillared montmorillonite) were performed (Lazar et al., 2009; Tomašević et al., 2007c, 2009c, 2010a, 2010b; Tomašević, 2011). The effect of catalyst type on the reaction is shown in Fig. 2. The photolysis of 16.22 mg/L of methomyl in different types of water (deionized, disstiled and sea water) at 254 nm was performed (Tomašević et al., 2009c, 2010a; Tomašević, 2011) and the influence of reaction parameters to degradation of pesticide were investigated. The studies showed that the photolysis reactions depend on the lamp distance (Fig. 3), water type (Fig. 4), reaction temperature and pH. The photocatalytic removal of the methomyl from aqueous solutions upon UV/Vis (366 and 300-400 nm) and natural solar light in the presence of TiO_2 and ZnO has been examined

(Tomašević et al., 2009b, 2010a; Tomašević, 2011) and the influence of reaction conditions (initial concentration of methomyl, catalysts type and concentration, pH, presence of Cl-ions) were studied. The results (Table 2) showed that the degradation of methomyl was much faster with ZnO than with TiO_2. The IC results confirmed that mineralization of methomyl led to the formation of sulfate, nitrate, and ammonium ions during the all investigated processes (Tomašević et al., 2010a, 2010b; Tomašević, 2011).
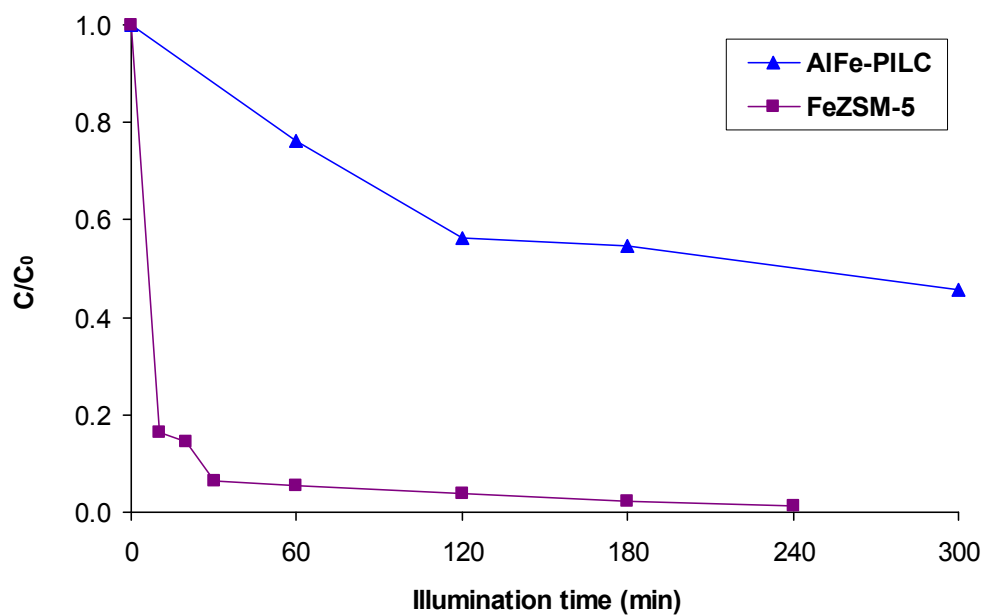

Fig. 2. Photodegradation of methomyl with 5 g/L of catalysts (Tomašević, 2011).
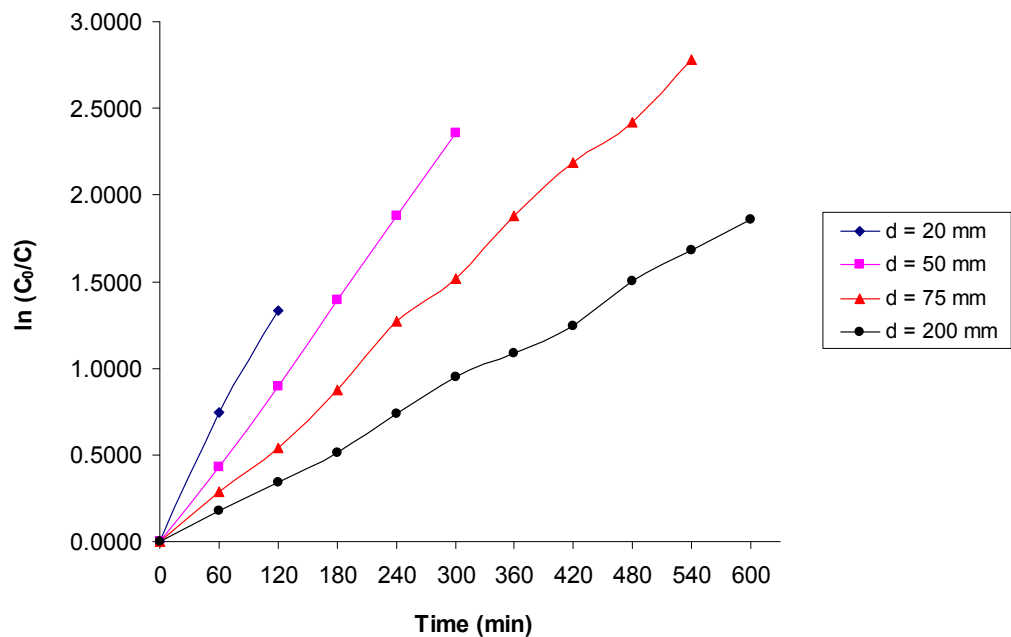
Fig. 3. The effect of lamp distance on the photolysis rate of methomyl (Tomašević, 2011).
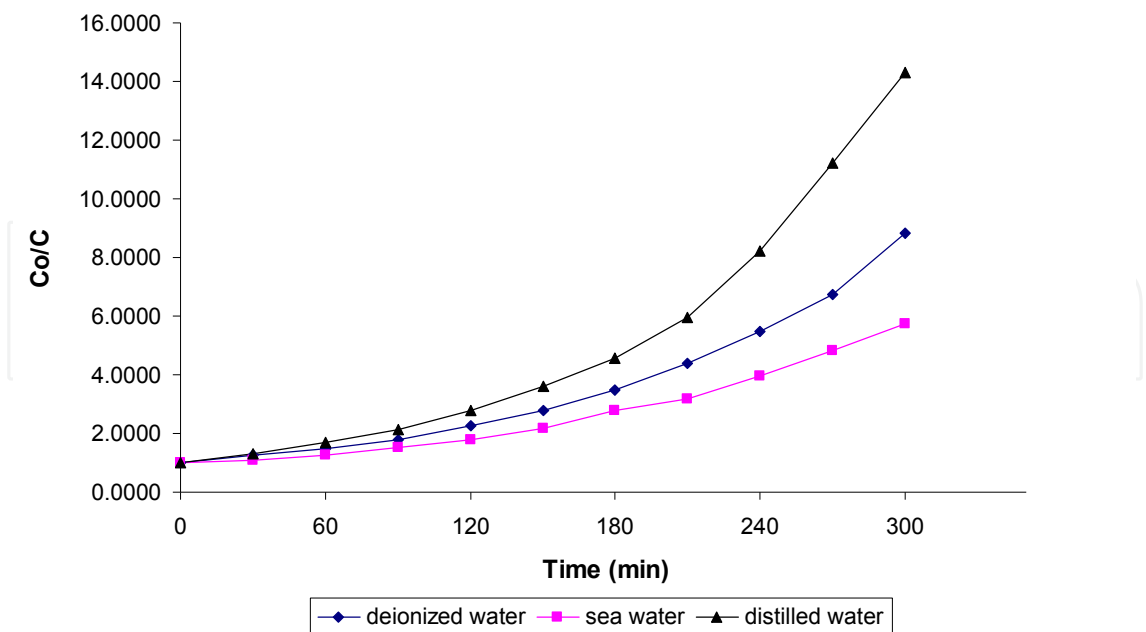
Fig. 4. The effect of the type of water on the photolysis rate of methomyl (Tomašević, 2011).

Technical methomyl	Parameters	Water type Deionized
With 2.0 g/L of TiO₂	k (min⁻¹)	0.0058
	R	0.9880
	t₁/₂ (min)	119.51
With 2.0 g/ L of ZnO	k (min⁻¹)	0.0120
	R	0.9915
	t₁/₂ (min)	57.76

Table 2. Kinetics of methomyl photodegradation at 366 nm (Tomašević, 2011).

4.10 Oxamyl

Oxamyl (IUPAC name: N,N-dimethyl-2-methylcarbamoyoxyimino-2-(methylthio) acetamide) is contact and systemic insecticide, acaricide and nematocide. It is used for control of chewing and sucking insects, spider mites and nematodes in ornamentals, frut trees, vegetables, cucurbits, beet, bananas, pineapples, peanuts, cotton, soya beans, tobacco, potatoes, and other crops. It could be found only as soluble concentrate (SL) on the market. The current regulation status of this active ingredient under directive 91/414/EEC is included in Annex 1, expiration of inclusion: 31/07/2016 (EU Pesticide Database, 2011; Tomlin, 2009).

An pre-industrial solar treatmen is used to prevent pollution of waters with commercial pesticide Vydate L, containing 24% oxamyl (Malato et al., 2000). Oxamyl is completely photodegraded, but mineralization is slow with illuminated TiO₂ only. The use of additional oxidants such as peroxydisulphate enhanced the degradation rate by a factor of 7 compared to TiO₂ alone. Solar photodegradation in aqueous solution of oxamyl in the presence of two photocatalysts TiO₂ and sodium decatungstate Na₄W₁₀O₃₂ is reported (Texier et al., 1999).

For pure compounds TiO_2 was a better catalyst than $Na_4W_{10}O_{32}$, concerning the rate of photodegradation and mineralization. When the pesticide is used as formulation product, the decatungstate anion becomes as efficien or even more efficient than TiO_2. This difference of reactivity is accounted for by the different nature of the active species during both photodegradation processes. The solar driven photo-Fenton process was applied to the degradation of oxamyl in the form of DuPont formulated product Vydate (Fallman et al., 1999). The obtained results shown that oxamyl was relatively recalcitrant (about 100 min was a TOC half-life and about 160 min was the time necessary for degradation of 80% of TOC).

4.11 Pirimicarb

Pirimicarb (IUPAC name: 2-dimethylamino-5,6-dimethylpyrimidin-4-yl dimethylcarbamate) is selective systemic insecticide with contact , stomach, and respiratory action. It is used as a selective aphicide for control a wide range of crops, including cereals, oil seeds, potatoes and other vegetables, ornamentals, and other non-food uses. Formulations types for this active ingredient are AE, DP, EC, FU, WG and WP. The current regulation status of this active ingredient under directive 91/414/EEC is included in Annex 1, expiration of inclusion: 31/07/2017 (EU Pesticide Database, 2011; Tomlin, 2009).

Photolysis of pirimicarb upon simulated solar light in natural water and in different aqueous solutions was investigated (Taboada et al., 1995). Aceton strongly increased degradation of pesticide, while methanol did not have any significant effect. The rate of pesticide degradation in the presence of river water was 4.5 times slower than in distilled water, and the half-life of pirimicarb in presence of dissolved humic and fulvic acids was 2-10 times longer than in distilled water. In all studied solutions the degradation reaction followed a first-order kinetics. The solar light and simulated sunlight were used for the photolysis of pirimicarb in water (Romero et al., 1994). The photodegradation mechanism seemed to be similar under both conditions, but the half-life of pirimicarb was found to be about three times longer under natural than under simulated conditions. Also, four main products were isolated and identified by spectroscopic methods. The photolysis of aqueous pirimicarb (3.3×10^{-3} M, 4 h, room temperature) has been examined by GC-MS (Climent & Miranda, 1996). Upon irradiation with 125 W medium-pressure mercury lamp three main photoproducts were detected.

4.12 Promecarb

Promecarb (IUPAC name: 3-methyl-5-methylphenyl methylcarbamate) is an obsolete carbamate insecticide once used to combat foliage and fruit eating insects. It is systemic insecticide. Promecarb is highly toxic by ingestion and is adsorbed through the skin. Formulations type is EC. The current regulation status of this active ingredient under directive 91/414/EEC is not included in Annex 1 (EU Pesticide Database, 2011; Tomlin, 2009).

The photolysis of promecarb in water solution (3.3×10^{-3} M, 4 h, room temperature, 125 W medium-pressure mercury lamp) has been examined by GC-MS (Climent & Miranda, 1996). Upon irradiation, 24% conversion of promecarb was achieved and photolysis of promecarb led to the phenol derivative (22%) as major product. Also, minor amounts of two compounds (isomers arising from photo-Fries rearrangement) were also obtained.

4.13 Propamocarb

Propamocarb (IUPAC name: propyl 3-(dimethylamino)propylcarbamate) is systemic fungicide with protective action. It is used for specific control of Phycomycetes. Also it is used against of wide variety of pest on tomatoes and potatoes, lettuce, cucumber, cabbages, ornamentals, fruit, vegetables, and vegetable seedbeds. Formulations types on the market are SC and SL. The current regulation status of this active ingredient under directive 91/414/EEC is included in Annex 1 expiration of inclusion: 30/09/2017 (EU Pesticide Database, 2011; Tomlin, 2009).

The application of solar photo-Fenton process for degradation of DuPont commercial product Previcur (Fallman et al., 1999) confirmed that propamocarb was one of the hardest pesticides to degrade by process (106 min was a TOC half-life and more than 200 min was the time necessary for degradation of 80% of TOC).

4.14 Propoxur

Propoxur (IUPAC name: 2-isopropoxyphenyl methylcarbamate) is non-systemic insecticide with contact and stomach action. It is used for control of cockroaches, flies, fleas, mosquitoes, bugs, ants, millipedes and other insect pests in food storage areas, houses, animal houses, etc. Also it is used for control of sucking and chewing insects (including aphids) in fruit, vegetables, ornamentals, vines, maize, alfalfa, soya beans, cotton, sugar cane, rice, cocoa, forestry, etc, and against migratory locusts and grasshoppers. There are a lot of different formulations with this active ingredient as AE, DP, EC, FU, GR, RB, SL, UL, WP and Oil spray. The current regulation status of this active ingredient under directive 91/414/EEC is not included in Annex 1 (EU Pesticide Database, 2011; Tomlin, 2009).

An study of the photodegradation of aerated aqueous propoxur solution is given very interesting data (Sanjuan et al., 2000). Photolysis of 1.0×10^{-3} M solution (pH 6.8) with 125 W medium-pressure mercury lamp leads to an almost complete degradation of pesticide and the formation of photo-Fries rearrangement products, but with a relatively minor degree of mineralization. Photocatalyzed degradations in the presence of TiO_2 (40 mg) or with 150 mg of triphenylpyrylium-Zeolite Y (TPY) were shown the same degree of propoxur mineralization. Laser flash photolysis (266 nm) has shown that the degradation could be initiated by a single electron transfer between excited 2,4,6-triphenylpyrylium cation and propoxur to form the corresponding 2,4,6-triphenylpyrylium radical and propoxur radical cation.

5. Conclusion

The reviewed literature reflects that in case of carbamate pesticides the most of the studies have been reported using photo-Fenton processes, photolysis and heterogeneous catalysis with TiO_2 as a catalyst. This photodegradation processes have been proposed as an effective and attractive techniques for degradation of carbamate residues in water. The kinetics of all photodegradation processes depend on several main parameters such as the nature of pesticides, type of light, initial concentration of pesticides (and catalysts), pH of solution, temperature, and presence of oxidant. The AOPs provide an excellent opportunity to use solar light as an energy source. Photocatalytic processes can lead to the mineralization of toxic and hazardous carbamate pesticides into carbon dioxide, water and inorganic mineral salts.

6. Acknowledgment

7. References

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Edited by Dr. Sonia Soloneski

It is our hope that this book will be of interest and use not only to scientists, but also to the food-producing industry, governments, politicians and consumers as well. If we are able to stimulate this interest, albeit in a small way, we have achieved our goal.

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